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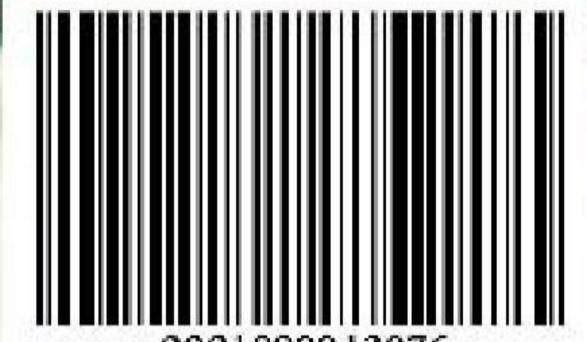
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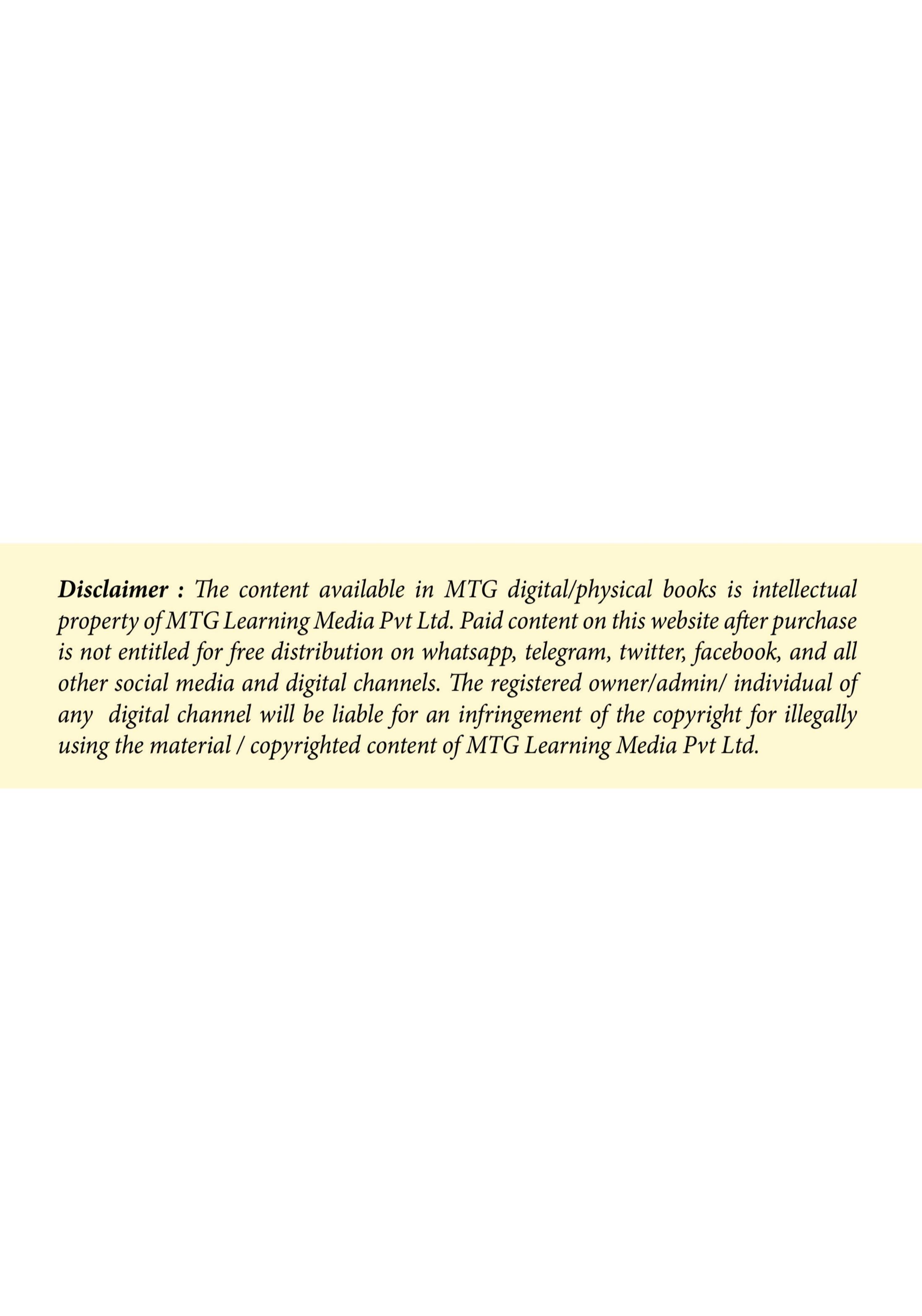


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#### Competition Edge

	JEE Main	4
Solved Pap	er Session 3	

11 NEET Practice Paper

18 JEE Advanced Practice Paper

**Concept Booster** 28

Chemistry of Substitution Reactions

#### Class 11

**Brush Up for NEET / JEE** 33

States of Matter: Gases & Liquids | Thermodynamics

45 **CBSE Warm Up** 

Redox Reactions | Hydrogen

#### Class 12

38 **Concept Map** 

Alcohols, Phenols and Ethers

**Brush Up for NEET / JEE** 53

Surface Chemistry | General Principles and Processes of Isolation of Elements

> 64 **CBSE Warm Up**

The p-Block Elements (Group 15 to 18) | Haloalkanes and Haloarenes

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### SOLVED PAPER

Held on 20<sup>th</sup> July, Morning Shift

#### **SECTION-A (MULTIPLE CHOICE QUESTIONS)**

- Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).
  - **Assertion** (A): Sharp glass edge becomes smooth on heating it upto its melting point.
  - **Reason** (R): The viscosity of glass decreases on melting.

Choose the most appropriate answer from the options given below.

- (a) A is false but R is true.
- (b) Both **A** and **R** are true but **R** is NOT the correct explanation of **A**.
- (c) A is true but R is false.
- (d) Both **A** and **R** are true and **R** is the correct explanation of **A**.
- Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

**Assertion** (A): The dihedral angles  $H_2O_2$  in gaseous phase is 90.2° and in solid phase is 111.5°.

**Reason** (R): The change in dihedral angle in solid and gaseous phase is due to the difference in the intermolecular forces.

Choose the most appropriate answer from the options given below for **A** and **R**.

- (a) Both **A** and **R** are correct but **R** is not the correct explanation of **A**.
- (b) **A** is correct but **R** is not correct.
- (c) Both **A** and **R** are correct and **R** is the correct explanation of **A**.
- (d) **A** is not correct but **R** is correct.
- 3. The set in which compounds have different nature is:
  - (a)  $Be(OH)_2$  and  $Al(OH)_3$
  - (b)  $B(OH)_3$  and  $Al(OH)_3$

- (c)  $B(OH)_3$  and  $H_3PO_3$
- (d) NaOH and Ca(OH)<sub>2</sub>
- 4. The correct structure of Rhumann's Purple, the compound formed in the reaction of ninhydrin with proteins is:

(a) 
$$N=N-N$$

(b) 
$$\bigcirc$$
 $N$ 
 $\bigcirc$ 
 $\bigcirc$ 
 $\bigcirc$ 
 $\bigcirc$ 
 $\bigcirc$ 
 $\bigcirc$ 

(c) 
$$N \longrightarrow N$$

$$(d) \bigcirc N - \bigcirc O$$

- 5. Green Chemistry in day-to-day life is in the use of:
  - (a) large amount of water alone for washing clothes
  - (b) liquified CO<sub>2</sub> for dry cleaning of clothes
  - (c) chlorine for bleaching of paper
  - (d) tetrachloroethene for laundry.

Which among the above compound/s does/do not form silver mirror when treated with Tollen's reagent?

- (a) Only (II)
- (b) Only(IV)
- (c) (III) and (IV) only (d) (I), (III) and (IV) only
- The metal that can be purified economically by fractional distillation method is:
  - (a) Ni
- (b) Fe
- (c) Cu
- (d) Zn
- Orlon fibres are made up of:
  - (a) cellulose
- (b) polyacrylonitrile
- (c) polyamide
- (d) polyesters.
- The species given below that does NOT show disproportionation reaction is:
  - (a) BrO<sup>-</sup>
- (b)  $BrO_2^-$
- (c)  $BrO_3^-$
- (d)  $BrO_4^-$
- 10. In the given reaction

3-Bromo-2,2-dimethylbutane 
$$\xrightarrow{C_2H_5OH}$$
 'A' (Major product)

#### Product 'A' is:

- (a) 2-Ethoxy-2,3-dimethyl butane
- (b) 2-Hydroxy-3,3-dimethyl butane
- (c) 1-Ethoxy-3,3-dimethyl butane
- (d) 2-Ethoxy-3,3-dimethyl butane

11. 
$$\underbrace{\begin{array}{c} \text{KMnO}_4 \\ \text{H}_2\text{SO}_4, \Delta \end{array}}_{\text{(major product)}} \overset{\text{A'}}{\text{(major product)}}$$

$$\begin{array}{c}
 & \text{KMnO}_4 \\
\hline
 & \text{H}_2\text{O}, 273 \text{ K} \\
\end{array}$$
(major product)

For above chemical reactions, identify the correct statement from the following.

- (a) Compound 'A' is diol and compound 'B' is dicarboxylic acid.
- (b) Both compound 'A' and compound 'B' are dicarboxylic acids.
- (c) Compound 'A' is dicarboxylic acid and compound 'B' is diol.
- (d) Both compound 'A' and compound 'B' are diols.

- **12.** Compound A is converted to B on reaction with CHCl<sub>3</sub> and KOH. The compound *B* is toxic and can be decomposed by *C*. *A*, *B* and *C* respectively are :
  - (a) secondary amine, isonitrile compound, conc. NaOH
  - (b) primary amine, isonitrile compound, conc. HCl
  - (c) primary amine, nitrile compound, conc. HCl
  - (d) secondary amine, nitrile compound, conc. NaOH.

13. 
$$\stackrel{\overset{+}{C}H_2}{\overset{+}{H_2}}$$
 $\stackrel{+}{\overset{+}{C}H_2}$ 
 $\stackrel{+}{\overset{+}{C}H_2}$ 
 $\stackrel{(A)}{\overset{+}{\overset{+}{C}H_2}}$ 
 $\stackrel{(B)}{\overset{+}{\overset{+}{C}H_2}}$ 
 $\stackrel{(C)}{\overset{+}{\overset{+}{C}H_2}}$ 

Among the given species the Resonance stabilised carbocations are:

- (a) (A), (B) and (C) only
- (b) (C) and (D) only
- (c) (A), (B) and (D) only
- (d) (A) and (B) only.
- 14. The correct order of intensity of colours of the compounds is:
  - (a)  $[Ni(H_2O)_6]^{2+} > [NiCl_4]^{2-} > [Ni(CN)_4]^{2-}$
  - (b)  $[NiCl_4]^{2-} > [Ni(CN)_4]^{2-} > [Ni(H_2O)_6]^{2+}$
  - (c)  $[NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+} > [Ni(CN)_4]^{2-}$
  - (d)  $[Ni(CN)_4]^{2-} > [NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+}$
- 15. According to the valence bond theory the hybridization of central metal atom is dsp<sup>2</sup> for which one of the following compounds?
  - (a)  $NiCl_2 \cdot 6H_2O$
- (b)  $K_2[Ni(CN)_4]$
- (c)  $[Ni(CO)_4]$
- (d)  $Na_2[NiCl_4]$
- 16. Identify the incorrect statement from the following:
  - (a) β-Glycosidic linkage makes cellulose polymer.
  - (b) Glycogen is called as animal starch.
  - (c) Starch is a polymer of α-D glucose.
  - (d) Amylose is a branched chain polymer of glucose.
- 17. A s-block element (M) reacts with oxygen to form an oxide of the formula  $MO_2$ . The oxide is pale yellow in colour and paramagnetic. The element (*M*) is:
  - (a) K
- (b) Mg
- (c) Na
- (d) Ca

- 18. Chemical nature of the nitrogen oxide compound obtained from a reaction of concentrated nitric acid and  $P_4O_{10}$  (in 4 : 1 ratio) is :
  - (a) amphoteric
- (b) neutral
- (c) acidic
- (d) basic.
- 19. An inorganic compound 'X' on treatment with concentrated H<sub>2</sub>SO<sub>4</sub> produces brown fumes and gives dark brown ring with FeSO<sub>4</sub> in presence of concentrated H<sub>2</sub>SO<sub>4</sub>. Also compound 'X' gives precipitate 'Y', when its solution in dilute HCl is treated with H<sub>2</sub>S gas. The precipitate 'Y' on treatment with concentrated HNO<sub>3</sub> followed by excess of NH<sub>4</sub>OH further gives deep blue coloured solution, compound 'X' is:
  - (a)  $Pb(NO_3)_2$
- (b)  $Pb(NO_2)_2$
- (c)  $Cu(NO_3)_2$
- (d)  $Co(NO_3)_2$
- **20.** The conditions given below are in the context of observing Tyndall effect in colloidal solutions :
  - (A) The diameter of the colloidal particles is comparable to the wavelength of light used.
  - (B) The diameter of the colloidal particles is much smaller than the wavelength of light used.
  - (C) The diameter of the colloidal particles is much larger than the wavelength of light used.
  - (D) The refractive indices of the dispersed phase and the dispersion medium are comparable.
  - (E) The dispersed phase has a very different refractive index from the dispersion medium.

Choose the most appropriate conditions from the options given below.

- (a) (C) and (D) only
- (b) (B) and (E) only
- (c) (A) and (D) only
- (d) (A) and (E) only

#### **SECTION-B (NUMERICAL VALUE TYPE)**

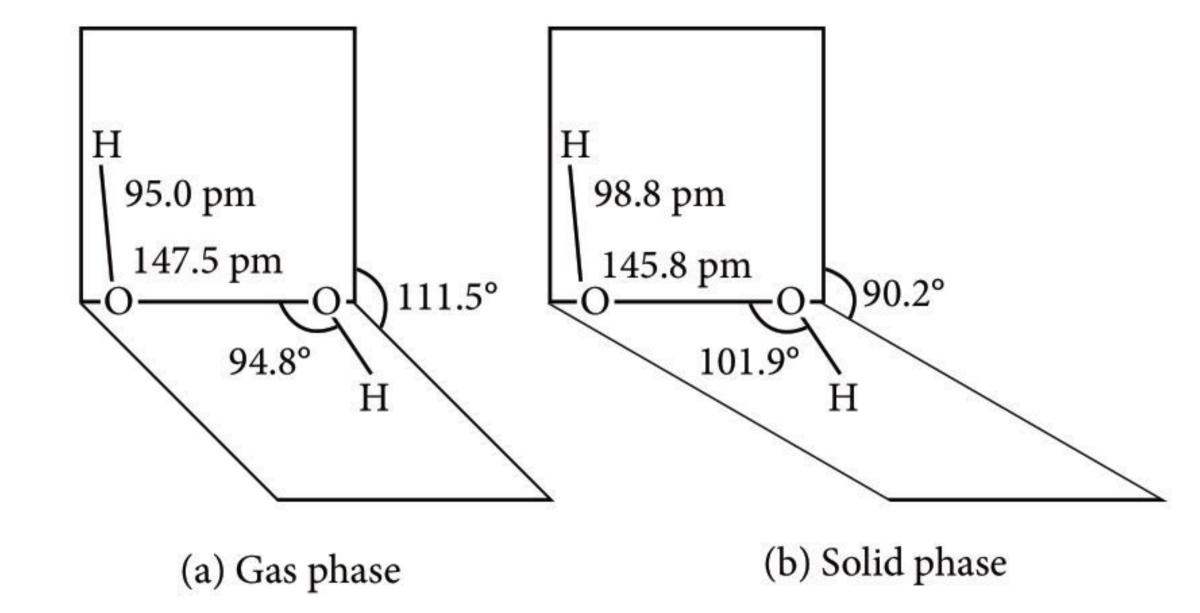
#### Attempt any 5 questions out of 10.

- 21. To synthesise 1.0 mole of 2-methylpropan-2-ol from Ethyl ethanoate \_\_\_\_\_ equivalents of CH<sub>3</sub>MgBr reagent will be required. (Integer value)
- 22. 250 mL of 0.5 M NaOH was added to 500 mL of 1 M HCl. The number of unreacted HCl molecules in the solution after complete reaction is  $\times 10^{21}$ . (Nearest integer)( $N_A = 6.022 \times 10^{23}$ )
- 23. An average person needs about 10000 kJ energy per day. The amount of glucose (molar mass =  $180.0 \text{ g mol}^{-1}$ ) needed to meet this energy requirement is \_\_\_\_\_ g. (Nearest integer) (Use :  $\Delta_c H$  (glucose) =  $-2700 \text{ kJ mol}^{-1}$ )

- 24. The number of nitrogen atoms in a semicarbazone molecule of acetone is \_\_\_\_\_.
- 25. The inactivation rate of a viral preparation is proportional to the amount of virus. In the first minute after preparation, 10% of the virus is inactivated. The rate constant for viral inactivation is \_\_\_\_\_ ×  $10^{-3}$  min<sup>-1</sup>. (Nearest Integer) [Use:  $\ln 10 = 2.303$ ;  $\log_{10} 3 = 0.477$ ; property of  $\log x^y = y \log x$ ]
- 26. At 20°C, the vapour pressure of benzene is 70 torr and that of methyl benzene is 20 torr. The mole fraction of benzene in the vapour phase at 20°C above an equimolar mixture of benzene and methyl benzene is  $\_\_\_$  ×  $10^{-2}$ . (Nearest Integer)
- 27. The number of lone pairs of electrons on the central I atom in  $I_3^-$  is \_\_\_\_\_.
- 28. The spin-only magnetic moment value for the complex  $[Co(CN)_6]^{4-}$  is \_\_\_\_\_ BM. [At. no. of Co = 27]
- 29.  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ In an equilibrium mixture, the partial pressure are  $p_{SO_3} = 43 \text{ kPa}$ ;  $P_{O_2} = 530 \text{ Pa}$  and  $p_{SO_2} = 45 \text{ kPa}$ . The equilibrium constant  $K_p = \underline{\hspace{1cm}} \times 10^{-2}$ . (Nearest Integer)
- 30. The Azimuthal quantum number for the valence electrons of Ga<sup>+</sup> ion is \_\_\_\_\_.
   (Atomic number of Ga = 31)

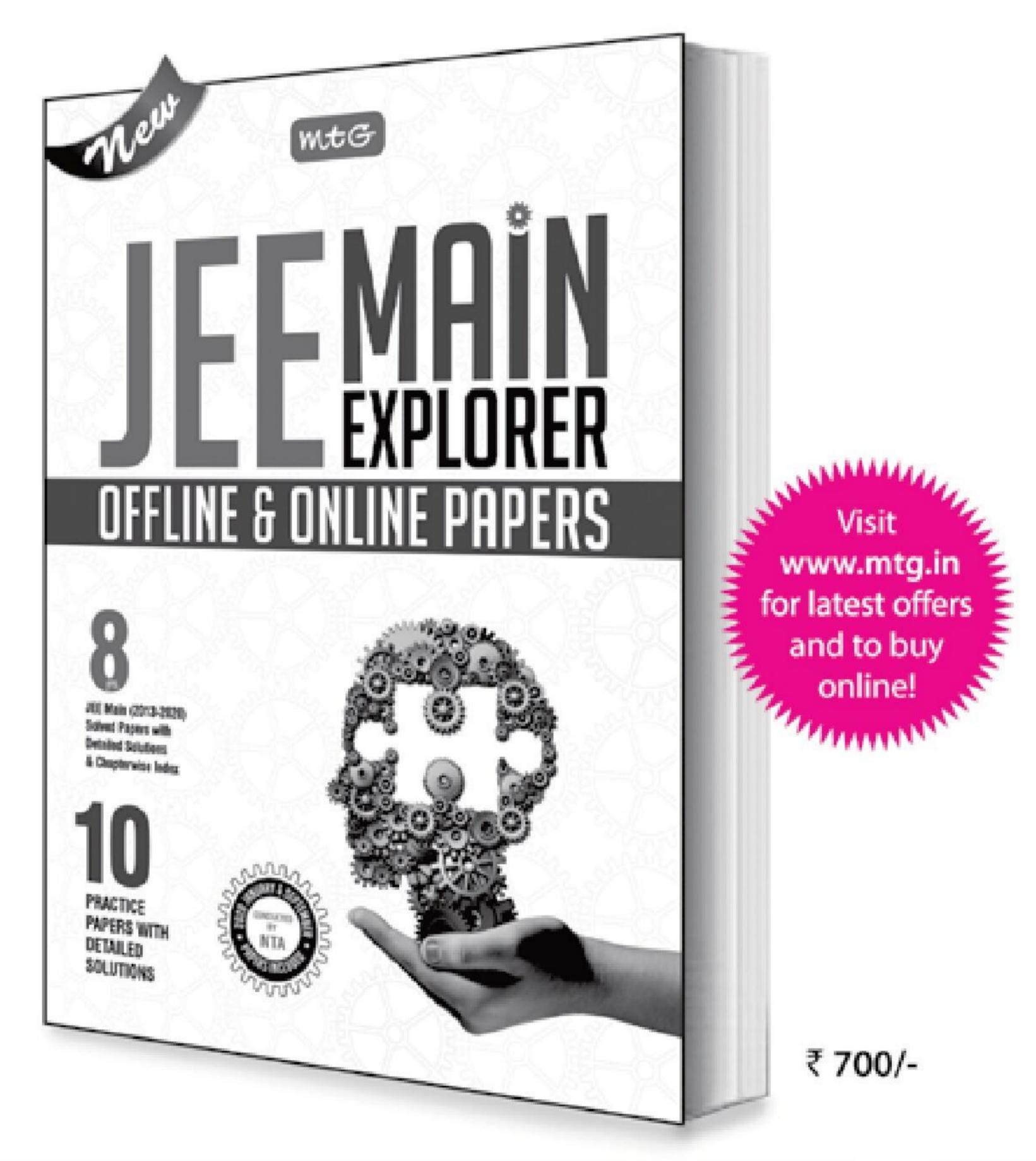
#### **SOLUTIONS**

- 1. (b): Sharp glass edge are heated to make them smooth because on heating glass melts and the surface of liquid tends to take the rounded shape at the edges which has minimum surface area. On heating viscosity decreases, but it is not related to smoothing of glass on heating.
- 2. (d):





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Available at all leading book shops throughout the country. To buy online visit www.mtg.in. For more information or for help in placing your order, call 0124-6601200 or email: info@mtg.in The dihedral angle of  $H_2O_2$  in gaseous phase is approximately 111.5° to minimize the repulsion between lone-pairs on oxygen and bonding pairs of -OH. While dihedral angle in solid  $H_2O_2$  is affected by hydrogen bonding and it is 90.2° in solid state.

3. (b): Be(OH)<sub>2</sub> and Al(OH)<sub>3</sub> – Amphoteric B(OH)<sub>3</sub> and H<sub>3</sub>PO<sub>3</sub> – Acidic NaOH and Ca(OH)<sub>2</sub> – Basic

Ninhydrin is useful for identification of  $\alpha$ -amino acids which react with ninhydrin to give deep blue colour.

- 5. (b): Tetrachloroethene ( $CCl_2=CCl_2$ ) was earlier used as solvent for dry cleaning agent but it is carcinogenic. So, liquid  $CO_2$  is used. Replacement of halogenated solvent by liquid  $CO_2$  will result in less harm to ground water.
- 6. (a): Aldehyde and hemiacetal groups form silver mirror when treated with Tollen's reagent. Hence, compounds (I), (III) and (IV) give this test.

7. (d): Fractional distillation process utilises the boiling point difference between metal and that of impurity. Using this process, crude zinc containing Cd, Fe and Pb as impurities can be refined.

8. (b): Orlon, also known as PAN is a polymer of acrylonitrile.

$$nCH_2 = CH - C = N \xrightarrow{Polymerisation} \begin{cases} CN \\ CH_2 - CH \end{cases}$$
Acrylonitrile

catalyst

Polyacrylonitrile

or orlon

9. (d): In  $BrO_4^-$ , Br is in maximum oxidation state *i.e.*, + 7. So, it can only reduce.

11 (c) Hot  $KMn\Omega$  in present

11. (c): Hot KMnO<sub>4</sub> in presence of H<sub>2</sub>SO<sub>4</sub> acts as strong oxidising agent. It reacts with alkenes to give dicarboxylic acid.

$$\begin{array}{c}
 & \text{KMnO}_4/\text{H}_2\text{SO}_4 \\
 & \Delta
\end{array}$$

$$\begin{array}{c}
 & \text{COOH} \\
 & \text{COOH}
\end{array}$$

KMnO<sub>4</sub> in water at room temperature is known as Bayer's reagent and it is a weak oxidising agent that gives diol on reacting with alkene.

$$\begin{array}{c}
 & \text{KMnO}_4/\text{H}_2\text{O} \\
\hline
 & 273 \text{ K}
\end{array}$$
OH

12. (b): Only primary amines give reaction with  $CHCl_3$  and KOH, known as carbylamine reaction.  $R-NH_2+CHCl_3+3KOH\rightarrow R-NC+3KCl_{1^\circ amine}$  Isonitrile  $+3H_2O$ 

1° amine Isonitrile 
$$+ 3H_{2}$$
(A) (Poisonous)
(B)
$$R - NC + HCl_{(Conc.)} \rightarrow R - NH_{2} + HCOOH$$

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13. (d): 
$$CH_2$$
 and  $H$  are resonance stabilised

carbocations because positive charge is in conjugation with double bond.

14. (c): As all complexes have Ni<sup>2+</sup>, so stronger is the ligand greater is the splitting and lighter is the colour.

Order of strength of ligand : Cl<sup>-</sup> < H<sub>2</sub>O < CN<sup>-</sup> So, order of intensity of colour:

$$[NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+} > [Ni(CN)_4]^{2-}$$

15. (b):	Complex	Hybridisation
	Na <sub>2</sub> [NiCl <sub>4</sub> ]	$sp^3$
	[Ni(CO) <sub>4</sub> ]	$sp^3$
	$K_2[Ni(CN)_4]$	$dsp^2$
	NiCl <sub>2</sub> ·6H <sub>2</sub> O	$sp^3d^2$

16. (d): Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000  $\alpha$ -D-(+)-glucose units held by C1-C4 glycosidic linkage.

17. (a): 
$$K + O_{2(excess)} \longrightarrow KO_2$$
  
Potassium on reaction with excess oxygen gives superoxide that is paramagnetic and pale yellow in colour.

18. (c):  $P_4O_{10} + 4HNO_3 \rightarrow 2N_2O_5 + 4HPO_3$ N<sub>2</sub>O<sub>5</sub> obtained is acidic in nature. It gives HNO<sub>3</sub> on dissolving in water.

19. (c): 
$$NO_3^- + H_2SO_4 \rightarrow NO_2^+ + H_2O$$
(X) (conc.) (Brown
(Anion) fumes)

FeSO<sub>4</sub> +  $H_2SO_4 + NO_3^- \rightarrow [Fe(H_2O)_5(NO)]SO_4$ 
(X) (Dark brown ring)

Cu<sup>2+</sup> + (dil. HCl +  $H_2S$ )  $\rightarrow$  CuS $\downarrow$ 

Black ppt.
(Y)

CuS 
$$\xrightarrow{\text{Conc. HNO}_3}$$
 Cu(NO<sub>3</sub>)<sub>2</sub> + NO<sub>2</sub> + S + H<sub>2</sub>O  
Excess NH<sub>4</sub>OH  $\rightarrow$  [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>
Deep blue

Hence, X is  $Cu(NO_3)_2$ .

- 20. (d): The conditions given below in the context of observing Tyndall effect in colloidal solutions are the following:
  - (A) The diameter of the colloidal particles is comparable to the wavelength of light used.
  - (E) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

21. (2): 
$$H_3C - C - O - C_2H_5 \xrightarrow{CH_3MgBr}$$

(Ethyl ethanoate)

O
(i)  $CH_3MgBr$ 
OH

 $H_3C - C - CH_3 \xrightarrow{(ii) H_3O^+} H_3C - C - CH_3$ 

CH<sub>2</sub>

2-Methylpropan-2-ol

22. (226): No. of moles of NaOH

$$= \frac{0.5 \times 250}{1000} = \frac{1}{8} = 0.125$$

No. of moles of HCl = 
$$\frac{1 \times 500}{1000} = \frac{1}{2} = 0.5$$

No. of moles of HCl unreacted = 0.5 - 0.125 = 0.375No. of molecules of HCl left unreacted  $= 0.375 \times 6.02 \times 10^{23} = 226 \times 10^{21}$ 

23. (667): 2700 kJ heat is produced by one mole of glucose.

No. of moles of glucose required for production of

10,000 kJ heat 
$$=\frac{10,000}{2700}$$
 mole

Total mass of glucose required

$$= \frac{10,000}{2700} \times 180 = 666.67 \approx 667 \text{ g}$$

25. (106): For first order reaction,

$$k = \frac{1}{t} \ln \left[ \frac{a}{a - x} \right]$$

$$= \frac{2.303}{1} \log \left[ \frac{100}{90} \right] = \frac{2.303}{1} \left[ \log 10 - 2 \log 3 \right]$$

$$= 2.303 \left[ 1 - 2 \times 0.477 \right] = 2.303 \times 0.046$$

$$= 0.1059 \text{ min}^{-1} = 105.9 \times 10^{-3} = 106 \times 10^{-3} \text{ min}^{-1}$$

26. (78):  $p_{\text{Total}} = p_{\text{Benzene}}^{\circ} x_{\text{Benzene}} + p_{\text{Toluene}}^{\circ} x_{\text{Toluene}}$ 

$$=(70)\frac{1}{2}+(20)\frac{1}{2}=35+10=45$$

 $p_{\text{Benzene}} = p_{\text{Total}} y_{\text{Benzene}}$ 

$$y_{\text{Benzene}} = \frac{70 \times \frac{1}{2}}{45} = \frac{35}{45} = 0.777 \approx 0.78 = 78 \times 10^{-2}$$

27. (3): 
$$\begin{bmatrix} I \\ I \\ I \end{bmatrix}$$

Total lone pairs on central atom = 3

28. (2):  $[Co(CN)_6]^{4-} \Rightarrow Co^{2+} \Rightarrow 3d^74s^0$ Since  $CN^-$  is a strong field ligand, so, complex formed will be low spin.

$$\frac{1}{1!} \frac{1}{1!} \frac{1}{t_{2\sigma}}$$

So, number of unpaired electrons = 1.

$$\mu = \sqrt{n(n+2)} = \sqrt{3}$$
  
 $\mu = 1.73 \text{ BM} \approx 2 \text{ BM}.$ 

29. (172): 
$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{O_2})} = \frac{(43)^2}{(45)^2(0.53)}$$
  
= 1.72 or 172 × 10<sup>-2</sup>

30. (0): Ga: 
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$$
  
Ga<sup>+</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ 

Valence electron is in s-orbital.

So, Azimuthal quantum number ( $\ell$ ) for valence shell electron is 0.



### Scientist of the Month

#### **Irène Joliot Curie**

#### **Early Life and Education**

Irène was born in Paris, France, in 1897 and was the first of Marie and Pierre's two daughters. Irène's education began at a school near the Observatory. In 1906, it was obvious, Irène was talented in mathematics and her mother chose to focus on that instead of public school. Marie joined forces with a number of eminent French scholars, including the prominent French physicist Paul Langevin to form "The Cooperative", which included



Irène Curie (12 September 1897 - 17 March 1956)

a private gathering of nine students that were children of the most distinguished academics in France. Each contributed to educating these children in their respective homes. The curriculum of The Cooperative was varied and included not only the principles of science and scientific research but such diverse subjects as Chinese and sculpture and with great emphasis placed on self-expression and play. Irène studied in this environment for about two years.

 Irène re-entered a more orthodox learning environment by going back to high school at the Collège Sévigné in central Paris until 1914. She then went onto the Faculty of Science at the Sorbonne to complete her baccalaureate, until 1916 when her studies were interrupted by World War I.

#### Contributions

 Irène Joliot Curie and her husband Frédéric combined their research efforts on the study of atomic nuclei and in 1932, they had full access to Marie's polonium. Experiments were done using gamma rays to identify

- the positron. Though their experiments identified both the positron and the neutron, they failed to interpret the significance of the results and the discoveries were later claimed by Carl David Anderson and James Chadwick respectively.
- In 1933, Joliot Curie and her husband were the first to calculate the accurate mass of the neutron.
- During an experiment of bombarding aluminium with alpha rays, they
  discovered that only protons were detected. Based on the undetectable
  electron and positron pair, they proposed that the protons changed into
  neutrons and positrons and later in october 1933, this new theory was
  presented to the Seventh Solvay Conference.
- In 1934, Joliot Curies finally made the discovery that sealed their place in scientific history. Irradiating the natural stable isotope of aluminium with alpha particles (i.e., helium nuclei) resulted in an unstable isotope of phosphorus: <sup>27</sup>Al + <sup>4</sup>He → <sup>30</sup>P + <sup>1</sup>n. This discovery is formally known as positron emission or beta decay, where a proton in the radioactive nucleus changes to a neutron and releases a positron and an electron neutrino. By then, the application of radioactive materials for use in medicine was growing and this discovery allowed radioactive materials to be created quickly, cheaply and plentifully.
- In 1948, using work on nuclear fission, Joliot Curie along with other scientists created the first French nuclear reactor.

#### Honors

- Nobel Prize in Chemistry in 1935 for the discovery of artificial radioactivity with Frédéric-Joliot Curie.
- Barnard Gold Medal for Meritorious Service to Science in 1940 with Frédéric-Joliot Curie.
- Officer of the Legion of Honor.
- Her name was added to the Monument to the X-ray and Radium Martyrs of All Nations erected in Hamburg, Germany.

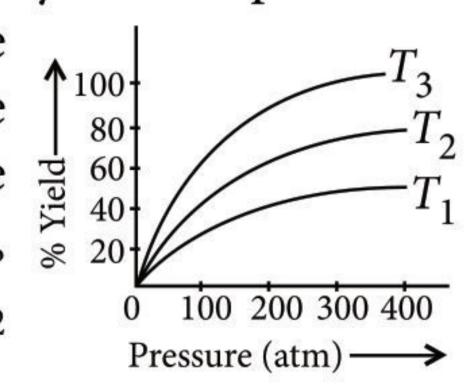
## PRACTICE PAPER

Exam on 12<sup>th</sup> September 2021

## 

#### **SECTION - A**

- What happens when the temperature of a solution is increased from 25°C to 65°C?
  - (a) The rate of the reaction remains unchanged and the rate constant *k* decreases.
  - (b) The rate of the reaction increases and rate constant *k* decreases.
  - (c) The rate of the reaction decreases and so does the rate constant *k*.
  - (d) The rate of the reaction increases and so does the rate constant *k*.
- 2. When LiNO<sub>3</sub> is heated, it gives oxide, Li<sub>2</sub>O, whereas other alkali metal nitrates decompose to give corresponding
  - (a) nitrite
  - (b) peroxide
  - (c) both nitrite and oxide
  - (d) none of these.
- Helium atom is two times heavier than a hydrogen molecule at 298 K. The average kinetic energy of helium is
  - (a) 2 times of  $H_2$  molecule
  - (b) same as that of  $H_2$  molecule
  - (c) 4 times that of hydrogen molecule
  - (d)  $\frac{1}{2}$  that of H<sub>2</sub> molecule.
- The preparation of ammonia by Haber's process is an exothermic reaction. If the precipitation follows the following temperature-pressure  $\frac{1}{2}$   $\frac{60}{40}$  relationship for its % yield,  $\frac{1}{2}$   $\frac{60}{40}$ then for temperatures  $T_1$ ,  $T_2$ and  $T_3$  the correct option is

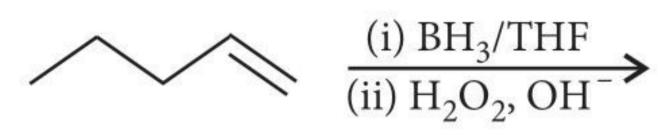


- (a)  $T_3 > T_2 > T_1$  (b)  $T_1 > T_2 > T_3$
- (c)  $T_1 = T_2 = T_3$
- (d) nothing could be predicted.

- Which of the following processes will convert starch directly into glucose?
  - (a) Heating with dilute  $H_2SO_4$ .
  - (b) Fermentation by diastase.
  - (c) Fermentation by zymase.
  - (d) Heating with dilute NaOH.
- The emf of a Daniell cell at 298 K is  $E_1$ Zn | ZnSO<sub>4</sub>(0.01 M) || CuSO<sub>4</sub> (1.0 M) | Cu When the concentration of ZnSO<sub>4</sub> is 1.0 M and that of CuSO<sub>4</sub> is 0.01 M, the emf is changed to  $E_2$ . What is the relationship between  $E_1$  and  $E_2$ ?
  - (a)  $E_2 = 0 \approx E_1$
- (b)  $E_1 > E_2$ 
  - (c)  $E_1 < E_2$
- (d)  $E_1 = E_2$
- The correct order of increasing basicity of the given conjugate bases ( $R = CH_3$ ) is
  - (a)  $RCOO^{-} < HC \equiv C^{-} < NH_{2}^{-} < R^{-}$
  - (b)  $RCOO^{-} < HC \equiv C^{-} < R^{-} < NH_{2}^{-}$
  - (c)  $R^- < HC \equiv C^- < RCOO^- < NH_2^-$
  - (d)  $RCOO^{-} < NH_{2}^{-} < HC \equiv C^{-} < R^{-}$
- Which set of quantum numbers is possible for the last electron of Mg<sup>+</sup> ion?
  - (a) n = 3, l = 2, m = 0, s = +1/2
  - (b) n = 2, l = 3, m = 0, s = +1/2
  - (c) n = 1, l = 0, m = 0, s = +1/2
  - (d) n = 3, l = 0, m = 0, s = +1/2
- 9. 2-Phenylethanol may be prepared by the reaction of phenyl magnesium bromide with
  - (a) HCHO
- (b) CH<sub>3</sub>CHO
- (c) CH<sub>3</sub>COCH<sub>3</sub>
- 10. One mole of a complex compound Co(NH<sub>3</sub>)<sub>5</sub>Cl<sub>3</sub> gives 3 moles of ions when dissolved in water. One mole of the same complex reacts with two moles of AgNO<sub>3</sub> solution to form two moles of AgCl. The structure of complex is
  - (a)  $[Co(NH_3)_5Cl]Cl_2$  (b)  $[Co(NH_3)_3Cl_3]\cdot 2NH_3$
  - (c)  $[Co(NH_3)_4Cl_2]Cl\cdot NH_3$
  - (d) none of these.

- 11. In a face centred cubic arrangement of A and B atoms, A atoms are at the corners of the unit cell and *B* atoms at the face centres. One of the *A* atoms is missing from one corner in the unit cell. The simplest formula of the compound is

  - (a)  $A_7B_3$  (b)  $AB_3$  (c)  $A_7B_{24}$  (d)  $A_{7/8}B_5$
- 12. The product of the following reaction is



- (a) 1-pentanol
- (b) 2-pentanol
- (c) pentane (d) 1,2-pentanediol.
- 13. The pH of 0.004 M hydrazine solution is 9.7. Its ionisation constant  $(K_h)$  is
  - (a)  $7.79 \times 10^{-8}$  (b)  $4.49 \times 10^{-9}$  (c)  $1.67 \times 10^{-10}$  (d)  $6.25 \times 10^{-7}$
- 14. Which of the following compounds does not give Tollens' test but gives DNP test and iodoform test?

(a) 
$$CH_3 - C - CH_2 - CH_3$$

- (b)  $CH_3-CH_2-C-CH_2-CH_3$
- (c)  $CH_3 CH_2 CHO$
- (d) CH<sub>3</sub>CHO
- 15. Which of the following are isoelectronic and isostructural?

- (a) NO<sub>3</sub>, ClO<sub>3</sub> (b) SO<sub>3</sub>, NO<sub>3</sub> (c) CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub> (d) Both (b) and (c)
- 16. Hybridisation in  $\dot{C}H_3$ ,  $\dot{C}H_3$  and  $\ddot{C}H_3$  are respectively
  - (a)  $sp^2$ ,  $sp^2$ ,  $sp^3$  (b)  $sp^2$ ,  $sp^3$ ,  $sp^3$

  - (c)  $sp^3$ ,  $sp^3$ ,  $sp^2$  (d)  $sp^3$ ,  $sp^2$ ,  $sp^2$
- 17. Major product of the following S<sub>N</sub>1 reaction is  $CH_3CHCHCH_3 + \bar{O}C_2H_5 \longrightarrow$

- (b) CH<sub>3</sub>CHCH<sub>2</sub>CH<sub>2</sub>OC<sub>2</sub>H<sub>5</sub> CH<sub>3</sub>
- (c) CH<sub>3</sub>CH<sub>2</sub>CCH<sub>3</sub> (d) none is correct.  $OC_2H_5$

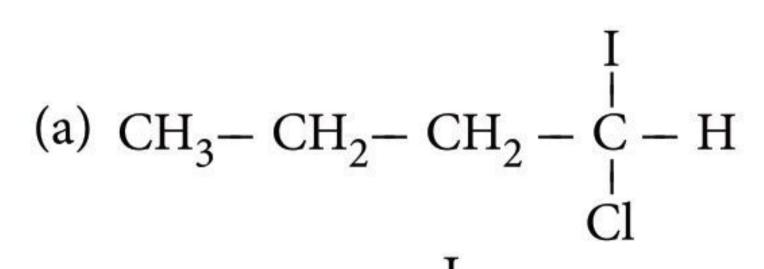
- 18. 1.00 g of a non-electrolyte solute (molar mass 250 g mol<sup>-1</sup>) was dissolved in 51.2 g of benzene. If the freezing point depression constant,  $K_f$  of benzene is 5.12 K kg mol<sup>-1</sup>, the freezing point of benzene will be lowered by
  - (a) 0.2 K (b) 0.4 K (c) 0.3 K (d) 0.5 K

- 19. Which of the following orders is true regarding the basic nature of NH<sub>2</sub> group?
  - (a) *o*-Toluidine > Aniline > *o*-Nitroaniline
  - (b) *o*-Toluidine < Aniline > *o*-Nitroaniline
  - (c) *o*-Toluidine < Aniline < *o*-Nitroaniline
  - (d) *o*-Toluidine > Aniline < *o*-Nitroaniline
- 20. The vapour density of a mixture containing NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> is 38.3 at 300 K. The number of moles of NO<sub>2</sub> in 100 g of the mixture is approximately
  - (a) 0.44
- (b) 4.4
- (c) 33.4
- (d) 3.34
- 21. Which of the following statements is incorrect?
  - (a) Anhydrous aluminium chloride cannot be prepared by heating AlCl<sub>3</sub>·6H<sub>2</sub>O because of hydrolysis of AlCl<sub>3</sub> into Al(OH)<sub>3</sub>.
  - (b) AlCl<sub>3</sub> is a high-melting solid while AlF<sub>3</sub> is a low-melting volatile solid.
  - (c) Aluminium forms  $[AlF_6]^{3-}$  ion but boron does not form  $[BF_6]^{3-}$ .
  - (d) Cryolite is added to alumina to lower the fusion temperature and to make the mass a good conductor of electricity.
- 22.  $K_{sp}$  of Fe(OH)<sub>3</sub> in aqueous solution is  $3.8 \times 10^{-38}$  at 298 K. The concentration of Fe<sup>3+</sup> will increase when
  - (a) pH is increased (b) pH is 7

  - (c) pH is decreased (d) it is exposed to air.
- 23. Which one of the following shows highest magnetic moment?
  - (a)  $V^{3+}$
- (c)  $Fe^{3+}$
- 24. The incorrect statement among the following is
  - (a) the first ionization potential of Al is less than the first ionization potential of Mg
  - (b) the second ionization potential of Mg is greater than the second ionization potential of Na
  - (c) the first ionization potential of Na is less than the first ionization potential of Mg
  - (d) the third ionization potential of Mg is greater than the third ionization potential of Al.
- 25. The number of alcohols that may have the molecular formula 'C<sub>4</sub>H<sub>10</sub>O' but do not have a chiral carbon is
  - (a) 1
- (b) 2
- (c) 3
- (d) 4

**26.** Predict the product C obtained in the following reaction of 1-butyne.

$$CH_3CH_2-C \equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$$



(b) 
$$CH_3 - CH_2 - CH - CH_2Cl$$

(c) 
$$CH_3 - CH_2 - CH_3 - CH_3$$

(d) 
$$CH_3 - CH - CH_2CH_2I$$
  
 $Cl$ 

- 27. The enthalpy of neutralisation of NH<sub>4</sub>OH and CH<sub>3</sub>COOH is -10.5 kcal mol<sup>-1</sup> and enthalpy of neutralisation of CH<sub>3</sub>COOH with strong base is -12.5 kcal mol<sup>-1</sup>. The enthalpy of ionisation of NH<sub>4</sub>OH will be
  - (a)  $4.0 \text{ kcal mol}^{-1}$  (b)  $3.0 \text{ kcal mol}^{-1}$  (c)  $2.0 \text{ kcal mol}^{-1}$  (d)  $3.2 \text{ kcal mol}^{-1}$

- 28. In the following reaction sequence,

$$C_7H_8 \xrightarrow{3Cl_2, \text{ heat}/h\nu} A \xrightarrow{Fe/Br_2} B \xrightarrow{Zn/HCl} C$$
the compound  $C$  is

- (a) 3-bromo-2,4,6-trichlorotoluene
- (b) *o*-bromotoluene
- (c) *p*-bromotoluene
- (d) *m*-bromotoluene.
- 29. The product of acid hydrolysis of *P* and *Q* can be distinguished by

$$H_2C = COCOCH_3 H_3C - OCOCH_3$$
 $P$ 
 $Q$ 
 $Q$ 
 $Q$ 

- (a) Lucas reagent
- (b) 2,4-DNP
- (c) Fehling's solution (d) NaHSO<sub>3</sub>
- **30.** XeF<sub>6</sub> on complete hydrolysis gives

  - (a)  $XeO_4$  (b)  $XeO_3$  (c)  $XeO_2$
- (d) Xe
- 31. The value of 'n' in the reaction,  $Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$ 
  - (a) 2

will be

- (b) 3 (c) 6
- (d) 7
- 32. Consider the following reactions (in gaseous phase) in equilibrium with equilibrium concentrations 0.1 M of every species
  - (I)  $2SO_2 + O_2 \Longrightarrow 2SO_3$
  - (II)  $N_2 + 3H_2 \implies 2NH_3$
  - (III)  $N_2O_4 \Longrightarrow 2NO_2$

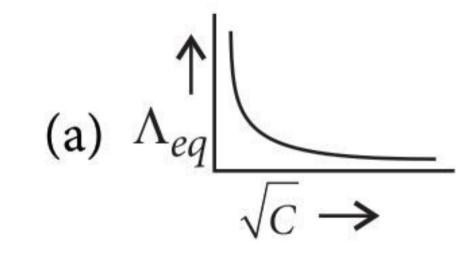
- (IV)  $4NO + 6H_2O \implies 4NH_3 + 5O_2$
- Extent of reaction will be in order
- (a)  $I = II \equiv III = IV$  (b) I = II = III < IV
- (c) III < I = IV < II (d) IV < III < I < II
- 33.  $CH_3OC_2H_5$  and  $(CH_3)_3C-OCH_3$  are treated with hydroiodic acid. The fragments obtained after reactions are respectively
  - (a)  $CH_3I + HOC_2H_5$ ;  $(CH_3)_3C I + HOCH_3$
  - (b)  $CH_3OH + C_2H_5I$ ;  $(CH_3)_3CI + HOCH_3$
  - (c)  $CH_3OH + C_2H_5I$ ;  $(CH_3)_3C OH + CH_3I$
  - (d)  $CH_3I + HOC_2H_5$ ;  $CH_3I + (CH_3)_3C OH$
- 34. Predict the product of reaction of  $I_2$  with  $H_2O_2$  in basic medium.
- (b)  $I_2O_3$  (c)  $IO_3^-$
- 35. Which of the following statements is incorrect?
  - (a) Brownian movement and Tyndall effect are shown by colloidal systems.
  - (b) Gold number is a measure of the protective power of a lyophillic colloid.
  - (c) The colloidal solution of a liquid in liquid is called gel.
  - (d) Hardy-Schulze rule is related with coagulation.

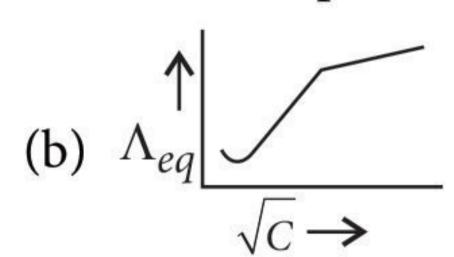
#### **SECTION - B**

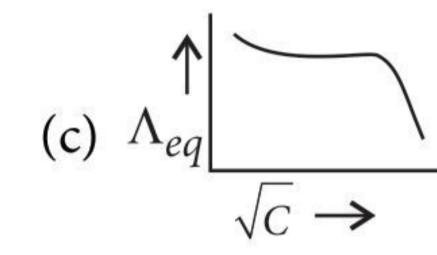
#### Out of 15 Questions, Attempt any 10 Questions

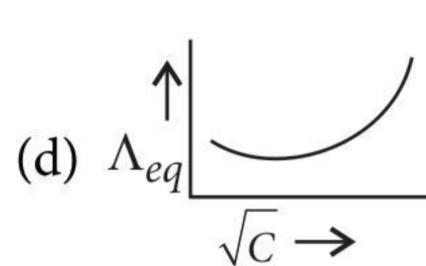
- 36. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?
  - (a) 0.16 mol/L
- (b) 0.31 mol/L
- (c) 0.60 mol/L
- (d) 0.45 mol/L
- 37. To prepare an ether by Williamson's synthesis, the reactants needed are
  - (a) ethyl alcohol and tert-butyl alcohol
  - (b) sodium ethoxide and tert-butyl bromide
  - (c) sodium *tert*-butoxide and ethyl bromide
  - (d) sodium ethoxide and sodium *tert*-butoxide.
- 38.  $Cr_2O_7^{2-} \xrightarrow{pH = x} CrO_4^{2-} \xrightarrow{pH = y} Cr_2O_7^{2-}$ pH values x and y can be
  - (a) 4 and 5
- (b) 4 and 8
- (c) 8 and 3
- (d) 8 and 9.
- 39. When one mole of a gas is heated at constant volume, temperature is raised from 298 to 308 K. Heat supplied to gas is 500 J. Then which of the following is correct?
  - (a)  $q = W = 500 \text{ J}, \Delta U = 0$
  - (b)  $q = \Delta U = 500 \text{ J}, W = 0$
  - (c)  $q = W = 500 \text{ J}, \Delta U = 500 \text{ J}$
  - (d)  $\Delta U = 0$ , q = W = -500 J

- 40. Which of the following are characteristics of thermosetting polymers?
  - I. Heavily branched cross linked polymers.
  - II. Linear slightly branched long chain molecules.
  - III. Become infusible on moulding so cannot be reused.
  - IV. Soften on heating and harden on cooling, can be reused.
  - (a) I and IV
- (b) II and III
- (c) I, II and III
- (d) I and III
- 41. Which one of the following statements is not true?
- (a) pH of drinking water should be between 5.5 - 9.5.
  - (b) Concentration of DO below 6 ppm is good for the growth of fish.
  - (c) Clean water would have a BOD value of less than 5 ppm.
  - (d) Oxides of sulphur, nitrogen and carbon are the most widespread air pollutants.
- **42.** The variation of equivalent conductance of a weak electrolyte with (concentration) is represented as

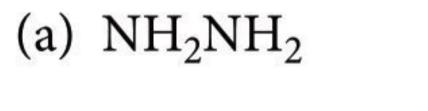


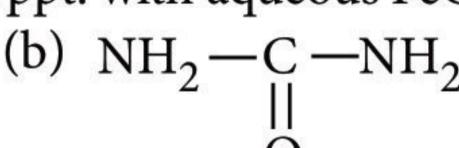






- 43. Which of the following statements is not true?
  - (a) Some disinfectants can be used as antiseptics at low concentration.
  - (b) Sulphadiazine is a synthetic antibacterial.
  - (c) Ampicillin is a natural antibiotic.
  - (d) Aspirin is both, an analgesic and an antipyretic.
- 44. Sodium extract of which of the following compounds does not form blood red ppt. with aqueous FeCl<sub>3</sub>?





- (d) Both (a) and (b)
- 45. Which method is not correctly given for refining of crude metals?
  - (a) Distillation: zinc and mercury.
  - (b) Liquation: tin.
  - (c) van Arkel: zirconium.
  - (d) Monds process: lead.

- **46.** Oxyacid with maximum P H bonds is
  - (a) hypophosphorous acid
  - (b) cyclotrimetaphosphoric acid
  - (c) hypophosphoric acid
  - (d) orthophosphorous acid.
- 47. The rate of reaction is equal to the rate constant, the order of reaction is
  - (a) 3
- (b) 0
- (c) 1
- (d) 2
- 48. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
  - (a) benzyl alcohol and sodium formate
  - (b) sodium benzoate and methyl alcohol
  - (c) sodium benzoate and sodium formate
  - (d) benzyl alcohol and methyl alcohol.
- 49. Which of the following does not have optical isomer?
  - (a)  $[Co(NH_3)_3Cl_3]$
- (b)  $[Co(en)_3]Cl_3$
- (c)  $[Co(en)_2Cl_2]Cl$  (d)  $[Co(en)(NH_3)_2Cl_2]Cl$
- 50. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is
  - (a) *p*-bromoaniline
- (b) *p*-bromofluorobenzene
- (c) 1, 3, 5-tribromobenzene
- (d) 2, 4, 6-tribromofluorobenzene.

#### SOLUTIONS

- 1. (d): With the increase of temperature, rate of reaction increases and thus rate constant also increases because rate  $\infty$  rate constant.
- 2. (a): When LiNO<sub>3</sub> is heated it gives oxide, NO<sub>2</sub> and O<sub>2</sub> while other nitrates of alkali metals give oxygen and nitrites.

 $4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ 

 $2MNO_3 \rightarrow 2MNO_2 + O_2$  (All Alkali metals except Li)

3. (b): Average kinetic energy =  $\frac{3}{2}kT$  where, k is

Boltzmann constant. Average kinetic energy is the same for all gaseous molecules.

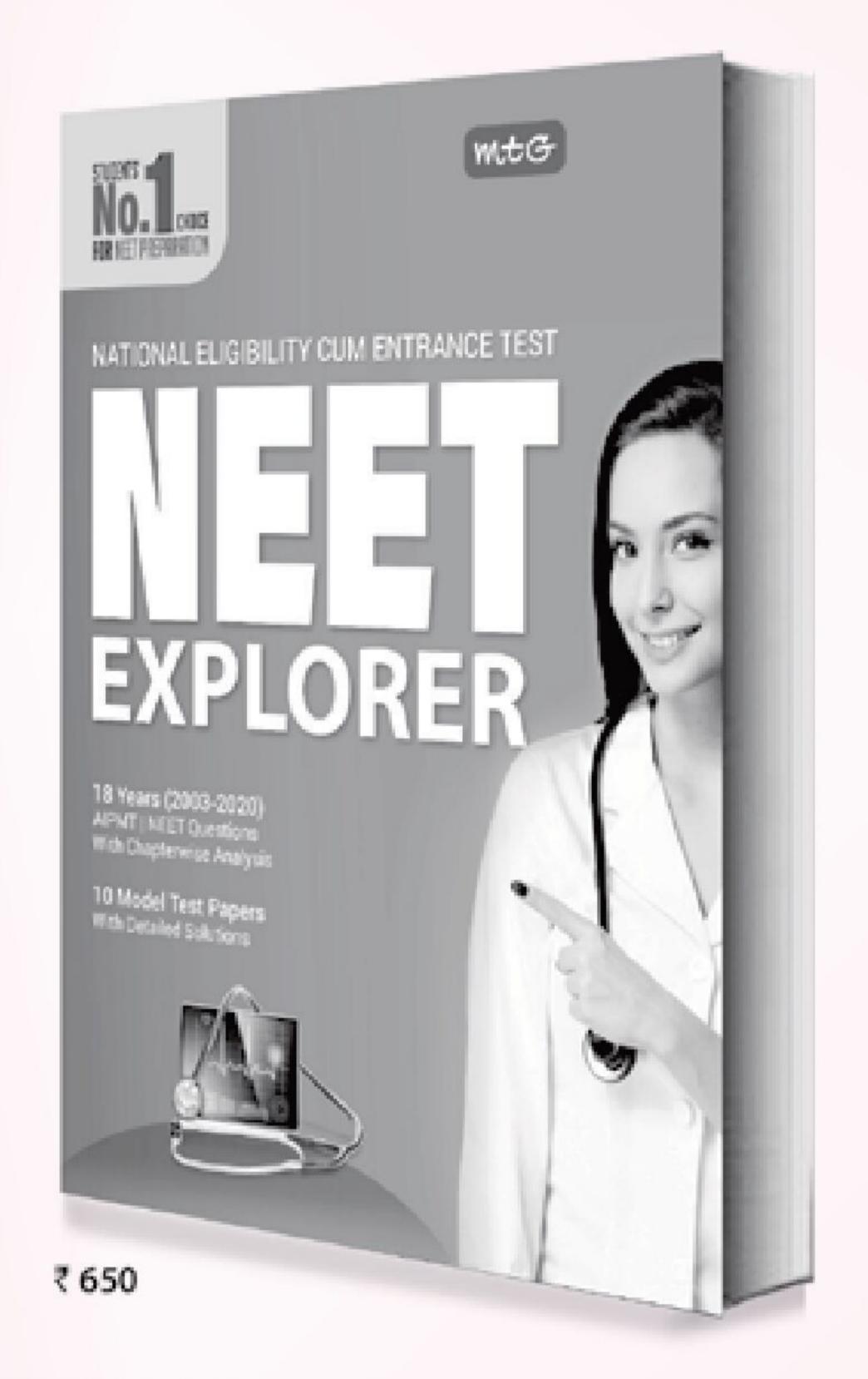
- 4. (b): For exothermic reactions as temperature increases yield decreases thus,  $T_1 > T_2 > T_3$ .
- **5.** (a)
- **6. (b)**: Daniell cell reaction:

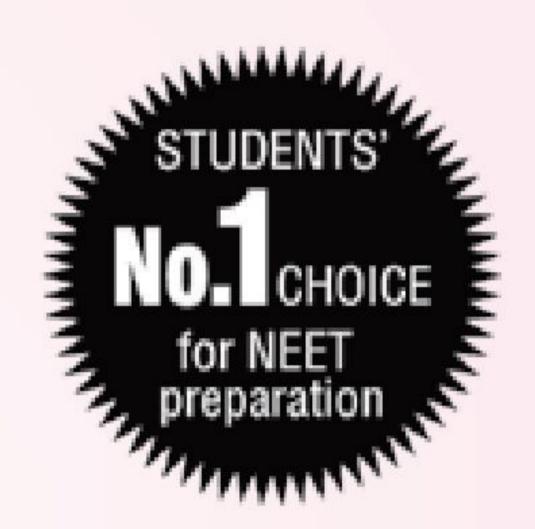
$$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$$
;  $n = 2$ 

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$



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$$E_1 = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{0.01}{1.0}$$

$$E_2 = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{1.0}{0.01}$$

On increasing  $[Zn^{2+}]$  and decreasing  $[Cu^{2+}]$ ,  $E_2$  becomes less than  $E_1$  *i.e.*,  $E_1 > E_2$ .

7. (a)

8. (d): Last electron of Mg<sup>+</sup> is  $3s^1$ . Mg: $1s^22s^22p^63s^2$ ; Mg<sup>+</sup>:  $1s^22s^22p^63s^1$ 

... For an  $e^-$  in 3s-orbital, the quantum numbers would be : n = 3, l = 0, m = 0, s = +1/2.

9. (d): 
$$C_6H_5MgBr + \sqrt{\frac{Ether}{D}}$$
  
Phenyl magnesium bromide

$$C_6H_5CH_2CH_2OMgBr \xrightarrow{H^+/H_2O} C_6H_5CH_2CH_2OH$$
2-Phenylethanol

10. (a) : Since the complex gives two moles of AgCl, there must be two ionisable chlorine atoms. Hence, compound should be  $[Co(NH_3)_5Cl]Cl_2$ .

$$[Co(NH3)5Cl]Cl2 + 2AgNO3 \longrightarrow [Co(NH3)5Cl](NO3)2 + 2AgCl \downarrow$$

$$[Co(NH_3)_5Cl]Cl_2 \xrightarrow{aq.} [Co(NH_3)_5Cl]^{2+} + 2Cl^{-}$$
Three ions

11. (c) : One atom of (A) is missing from one corner. No. of atoms A in unit cell =  $7 \times 1/8 = 7/8$ No. of atoms B in unit cell =  $6 \times 1/2 = 3$ A: B = 7/8: 3 so, simplest formula is  $A_7B_{24}$ .

12. (a): Hydroboration - oxidation leads to anti - Markownikoff's hydration,

1-Pentene (i) 
$$\frac{\text{Harkovillikolity of Hydrations,}}{\text{(ii) H}_2\text{O}_2, \text{OH}}$$
OH

1-Pentene

1-Pentanol

13. (d): For weak bases:  $[OH^-] = \sqrt{K_h \times C}$ 

pH = 9.7 thus, pOH = 
$$14 - 9.7 = 4.3$$
  
-log[OH<sup>-</sup>] =  $4.3$ 

$$\Rightarrow [OH^-] = 5 \times 10^{-5}$$

$$5 \times 10^{-5} = \sqrt{K_b \times 0.004}$$
 or  $K_b \times 0.004 = 25 \times 10^{-10}$ 

$$\Rightarrow K_b = \frac{25}{4 \times 10^{-3}} \times 10^{-10} = 6.25 \times 10^{-7}$$

14. (a): Only aldehydes give positive tollen's test while both aldehydes and ketones given DNP test positive.

17. (c)

18. (b): 
$$m = \frac{1000 \times K_f \times w}{W \times \Delta T}$$
 or  $250 = \frac{1000 \times 5.12 \times 1}{51.2 \times \Delta T}$ 

$$\Delta T = \frac{1000 \times 5.12 \times 1}{51.2 \times 250} = 0.4 \text{ K}$$

19. (b)

20. (a): Molecular weight of the mixture =  $38.3 \times 2$ = 76.6

Let mass of  $NO_2$  in the mixture = x g

then mass of  $N_2O_4 = (100 - x)$  g

Number of moles of  $NO_2 = x/46$ 

Number of moles of  $N_2O_4 = 100-x/92$ 

(Molecular weight of  $NO_2 = 46$ , Molecular weight of  $N_2O_4 = 92$ )

Weight

Number of moles = Molecular weight

$$\frac{x + (100 - x)}{\frac{x}{46} + \frac{(100 - x)}{92}} = 76.6 \Rightarrow \frac{x}{46} + \frac{(100 - x)}{92} = \frac{100}{76.6}$$
$$x = 20.1$$

Number of moles of NO<sub>2</sub> =  $\frac{20.1}{46}$  = 0.437  $\approx$  0.44

21. (b)

22. (c)

23. (c)

**24.** (b) :  $IE_2$  of Mg is lower than that of Na because in case of Mg<sup>+</sup>, one *s*-electron has to be removed where in case of Na<sup>+</sup>, an electron is to be removed from the stable inert gas configuration which is difficult.

26. (c) : 
$$CH_3 - CH_2 - C \equiv CH + HCl \longrightarrow I$$

$$CH_3 - CH_2 - C = CH_2 \xrightarrow{HI} CH_3 - CH_2 - C - CH_3$$

$$Cl$$

$$(B)$$

$$(C)$$

According to Markownikoff's rule, during hydrohalogenation to unsymmetrical alkene, the negative part of the addendum adds to less hydrogenated (*i.e.*, more substituted) carbon atom.

27. (c) :  $\Delta H_{\text{neut}}$  for a strong acid with a strong base = -13.7 kcal equiv<sup>-1</sup> = -13.7 kcal mol<sup>-1</sup>

(For monovalent acids and bases)

$$\Delta H_{\text{ion}} (\text{CH}_3\text{COOH}) = -12.5 - (-13.7) = +1.2 \text{ kcal mol}^{-1}$$
  
 $\Delta H_{\text{ion}} (\text{NH}_4\text{OH}) = -10.5 - (-13.7) - \Delta H_{\text{ion}} (\text{CH}_3\text{COOH})$   
 $= 13.7 - 10.5 - 1.2 = 2 \text{ kcal mol}^{-1}$ 

30. (b): XeF<sub>6</sub> on complete hydrolysis yields xenon trioxide, XeO<sub>3</sub>.

 $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$ 

31. (c)

32. (c): Equilibrium concentration is 0.1 M in each case. Greater the value of  $K_c$ , greater is the extent of reaction.

33. (a)

34. (a):  $I_2 + H_2O_2 \xrightarrow{OH^-} 2I^- + H_2O + O_2$ 

35. (c): Liquid-liquid system is known as emulsion.

**36.** (b) :  $\pi = CRT$ 

$$C = \frac{\pi}{RT} = \frac{7.8}{0.082 \times 310} = 0.31 \text{ mol/L}$$

37. (c): 1° alkyl halides on treatment with an alkoxide ion tend to undergo substitution to form ethers. So, sodium *tert*-butoxide and ethyl bromide reagent is used.

38. (c) :  $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$ ; pH > 7 (x > 7)

 $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O; pH < 7 (y < 7)$ 

39. (b): As volume is constant,  $\Delta V = 0$ 

 $W = -P\Delta V = 0$ 

 $\Delta U = q + W$ ;  $\Delta U = 500 \text{ J} + 0$  :  $\Delta U = q = +500 \text{ J}$ 

40. (d)

41. (b): Fishes die in water bodies having low level of dissolved oxygen (DO).

42. (a): The equivalent conductance of weak electrolytes increases steeply with dilution especially in the low concentration region.

43. (c): Ampicillin is a synthetic modification of penicillin.

44. (d): Compound with N, S and carbon will form NaSCN to give red ppt.

45. (d): Mond's process is used for nickel.

**47. (b)**:  $r = k[A]^x \implies x = 0$  when r = k

48. (a): A mixture of benzaldehyde and formaldehyde undergoes cross Cannizzaro reaction.

 $C_6H_5CHO + HCHO \xrightarrow{NaOH} C_6H_5CH_2OH + HCOONa$ 

49. (a) : Octahedral complexes of type  $[MA_3B_3]$  does not show optical isomerism.

50. (d)

2626

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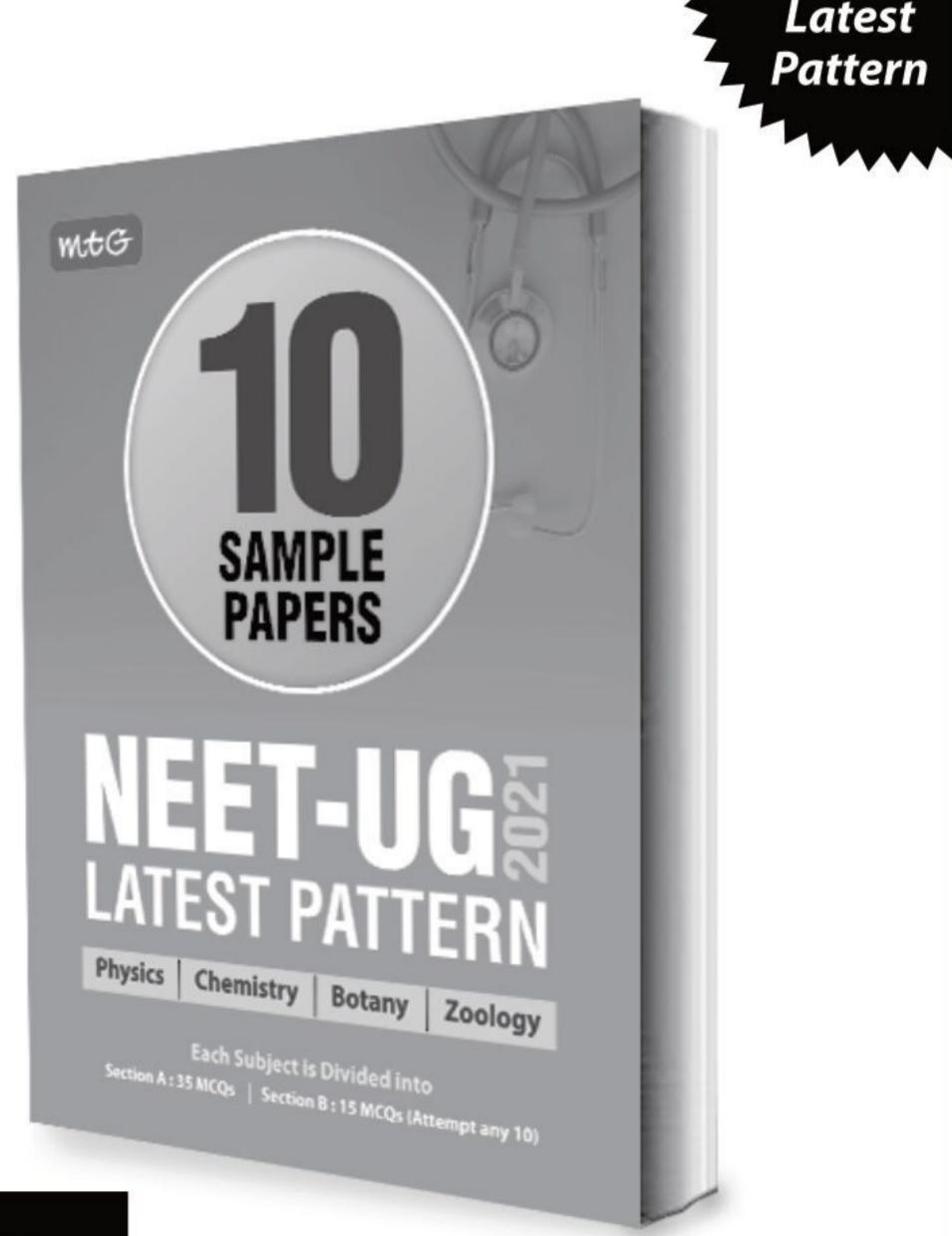
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## 2021

Exam on 3<sup>rd</sup> October 2021

## ADVANGED

#### PAPER - I

#### Section 1 (Maximum Marks: 18)

- This section contains SIX (06) questions.
- Each question has FOUR options. ONLY ONE of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks:

+3 If ONLY the correct option is chosen.

Zero Marks:

0 If none of the options is chosen (i.e., the question is unanswered).

Negative Marks: -1 In all other cases.

- 1. In which of the following sequence of reaction the end product does not exhibit tautomerism?
  - (a)  $CH_3CH_2NH_2 \xrightarrow{NOCl} AgNO_2 \rightarrow$
  - (b)  $(CH_3)_2CHNH_2 \xrightarrow{NOCl} AgNO_2 \rightarrow$
  - (c)  $(CH_3)_3CNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$
  - (d)  $CH_3CH(NH_2)C_2H_5 \xrightarrow{NOCl} AgNO_2 \rightarrow$
- Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

$$\begin{array}{c} \text{XeF}_6 \xrightarrow{\text{Complete hydrolysis}} P + \text{other product} \\ & \downarrow \text{OH}^-\text{/H}_2\text{O} \\ & Q \\ & \downarrow \text{slow disproportionation} \\ & \text{in OH}^-\text{/H}_2\text{O} \\ & \text{products} \end{array}$$

- (a) 0
- (b) 1
- (c) 2
- (d) 3
- The freezing point of 0.02 mole fraction solution of acetic acid in benzene is 277.4 K. Assuming molality equal to molarity, calculate  $K_c$  for the equilibrium reaction,  $2CH_3COOH \rightleftharpoons (CH_3COOH)_2$ [Given  $T_f$  (benzene) = 278.4 K and  $K_f$  (benzene)  $= 5.0 \text{ K kg mol}^{-1}.$ 
  - (a)  $1.532 \text{ M}^{-1}$
- (b)  $0.685 \text{ M}^{-1}$
- (c)  $2.794 \text{ M}^{-1}$
- (d)  $0.032 \text{ M}^{-1}$

The following tripeptide can be synthesized from the following amino acids:

- (a) Glycine, Leucine and Alanine
- (b) Alanine, Isoleucine and Glycine
- (c) Valine, Alanine and Glycine
- (d) Alanine, Serine and Glycine
- Among  $[Ni(CO)_4]$ ,  $[NiCl_4]^{2-}$ ,  $[Co(NH_3)_4Cl_2]Cl$ , Na<sub>3</sub>[CoF<sub>6</sub>], Na<sub>2</sub>O<sub>2</sub> and CsO<sub>2</sub>, the total number of paramagnetic compounds is
  - (a) 2
- (b) 3
- (c) 4
- (d) 5

inactive)

Identify (A) in the above reaction sequence.

- (a)
- (b)  $CH_3 C \equiv C CH_3$
- (c)  $H_2C = CH CH = CH_2$
- (d)  $CH_3CH_2C \equiv CH$

#### Section 2 (Maximum Marks : 24)

- This section contains SIX (06) questions.
- Each question has FOUR options. ONE OR MORE THAN ONE of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:
  - Full Marks:
- +4 If only (all) the correct option(s) is (are) chosen.
- Partial Marks:
  - +3 If all the four options are correct but ONLY three options are
  - chosen.
- Partial Marks:
- +2 If three or more options are correct but ONLY two options are chosen, both of which are correct.

Partial Marks: +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.

Zero Marks: 0 If none of the options is chosen (i.e., the question is unanswered).

Negative Marks: -2 In all other cases.

- 7. Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $MCl_2 \cdot 6H_2O(X)$  and  $NH_4Cl$  gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1:3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. Among the following options, which statement(s) is(are) correct?
  - (a) The hybridization of the central metal ion in Y is  $d^2sp^3$ .
  - (b) When X and Z are in equilibrium at 0°C, the colour of the solution is pink.
  - (c) Z is a tetrahedral complex.
  - (d) Addition of silver nitrate to *Y* gives only two equivalents of silver chloride.
- 8. Which of the following reactions are correctly interpreted?

(a) 
$$(CH_3)_3C - CH = CH_2 + Hg(OAc)_2 \xrightarrow{NaBH_4} (CH_3)_3C - CH_2CH_2OH$$

(b) 
$$\bigcirc CH_3 CH_3$$
 $\downarrow CH_3 CH_3$ 
 $\downarrow CH_3 CH_3$ 
 $\downarrow CH_3 CH_3$ 
 $\downarrow CH_3 CH_3$ 
 $\downarrow CH_3 CH_3$ 
(c)  $\bigcirc CH_3 CH_3$ 
 $\bigcirc CH_3 CH_2$ 
 $\bigcirc CH_3 CH_2$ 
 $\bigcirc CH_3 CH_3$ 
(d)  $\bigcirc CH_3 CH_2$ 
 $\bigcirc CH_3 CH_3$ 
 $\bigcirc CH_3 CH_3$ 
 $\bigcirc CH_3 CH_3$ 
 $\bigcirc CH_3 CH_3$ 
 $\bigcirc CH_3 CH_3$ 

- 9. Among the following, the correct statement(s)is(are)
  - (a)  $Al(CH_3)_3$  has the three-centre two-electron bonds in its dimeric structure
  - (b) BH<sub>3</sub> has the three-centre two-electron bonds in its dimeric structure
  - (c) the Lewis acidity of BCl<sub>3</sub> is greater than that of AlCl<sub>3</sub>
  - (d) AlCl<sub>3</sub> has the three-centre two-electron bonds in its dimeric structure.

- **10.** Reagent which cannot be used to distinguish allyl bromide from *n*-propyl bromide is/are
  - (a)  $Br_2/CCl_4$
  - (b) shaking with an aqueous solution of AgNO<sub>3</sub>
  - (c) boiling with aqueous KOH solution followed by acidification with dil. HNO<sub>3</sub> and addition of AgNO<sub>3</sub> solution
  - (d) fusion with Na followed by acidification with dilute HNO<sub>3</sub> and addition of AgNO<sub>3</sub> solution.
- 11. Which of the following are arranged in correct order as indicated?

[Nucleophilic addition reaction]

(b)  $CH_3COCl > (CH_3CO)_2O > CH_3COOCH_3$ >  $CH_3CO\ddot{N}H_2$ 

[Acyl S<sub>N</sub>2 reaction]

- (c) CH<sub>3</sub>CH<sub>2</sub>COOH > CH<sub>3</sub>COOH > HCOOH [Rate of esterification reaction]
- (d) CH<sub>3</sub>COOCH<sub>3</sub> > CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> > CH<sub>3</sub>COOC<sub>3</sub>H<sub>7</sub> [Rate of hydrolysis]
- 12. Out of the following pairs of electrons, identify the pairs of electrons present in degenerate orbitals:

(a) (i) 
$$n = 3$$
,  $l = 2$ ,  $m_l = -2$ ,  $m_s = -\frac{1}{2}$ 

(ii) 
$$n = 3$$
,  $l = 2$ ,  $m_l = -1$ ,  $m_s = -\frac{1}{2}$ 

(b) (i) 
$$n = 3, l = 1, m_l = 1, m_s = +\frac{1}{2}$$

(ii) 
$$n = 3$$
,  $l = 2$ ,  $m_l = 1$ ,  $m_s = +\frac{1}{2}$ 

(c) (i) 
$$n = 4$$
,  $l = 1$ ,  $m_l = 1$ ,  $m_s = +\frac{1}{2}$ 

(ii) 
$$n = 3$$
,  $l = 2$ ,  $m_l = 1$ ,  $m_s = +\frac{1}{2}$ 

(d) (i) 
$$n = 3$$
,  $l = 2$ ,  $m_l = +2$ ,  $m_s = -\frac{1}{2}$ 

(ii) 
$$n = 3$$
,  $l = 2$ ,  $m_l = +2$ ,  $m_s = +\frac{1}{2}$ 

#### Section 3 (Maximum Marks: 24)

- This section contains SIX (06) questions. The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme:

+4 If ONLY the correct numerical Full Marks: value is entered.

In all other cases. Zero Marks:

- 13. An aqueous solution of a metal bromide  $MBr_2$  (0.05 M) is saturated with H<sub>2</sub>S. What is the minimum pH at which MS will precipitate?  $K_{sp}$  for  $MS = 6.0 \times 10^{-21}$ . Concentration of saturated  $\hat{H}_2S = 0.1 \text{ M}$ ;  $K_1 = 10^{-7}$ and  $K_2 = 1.3 \times 10^{-13}$  for H<sub>2</sub>S.
- 14. Two drops of phenolphthalein solution was added to 40.00 mL of an HCl solution, and this solution was titrated with 0.1000 M NaOH. When 30.00 mL of base had been added, part of the solution turned pink, but the colour disappeared upon mixing the solution. Addition of NaOH solution was continued dropwise until a one drop addition produced a lasting pink colour. At this point the volume of base added was 32.56 mL. What was the concentration (in molarity) of the HCl solution?

15. The standard emf of the cell  $Cd_{(s)} | CdCl_{2(aa)} (0.1 M) | | AgCl_{(s)} | Ag_{(s)}$ is 0.6915 V at 0°C and 0.06573 V at 25°C in which the cell reaction is

 $Cd_{(s)} + 2AgCl_{(s)} \rightarrow 2Ag_{(s)} + Cd_{(aq)}^{2+} + 2Cl_{(aq)}^{-}$ . The enthalpy change of the reaction at 25°C is \_\_\_\_\_ kJ.

(i) HCHO (excess)/NaOH, heat 16. (ii) HCHO/H<sup>+</sup> (catalytic amount)

Sum of carbon and oxygen atoms in the major product of above reaction is\_\_\_\_\_.

- 17. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings  $(\Delta S_{surr})$  in J K<sup>-1</sup> is -x. Value of x is \_\_\_\_\_. (1 L atm = 101.3 J)
- 18.  $C_9H_{12}O(A)$  rotates the plane polarised light, evolves H<sub>2</sub> with Na metal, reacts with I<sub>2</sub> and NaOH to produce yellow ppt. of CHI<sub>3</sub>. It reacts with Lucas reagent in five minutes. It does not react with Br<sub>2</sub>/CCl<sub>4</sub>. It reacts with hot KMnO<sub>4</sub> to form compound (B)  $C_7H_6O_2$  which can be obtained by reaction of benzene with carbonyl chloride in presence of AlCl<sub>3</sub>, followed by hydrolysis. (A) loses optical activity as a result of formation of compound (C) on being heated with HI and red P. Calculate the molecular weight of (C).

#### PAPER - II

#### Section 1 (Maximum Marks: 18)

- This section contains SIX (06) questions.
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, BOTH INCLUSIVE.
- For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks: +3 If ONLY the correct integer is entered.

If the question is unanswered; Zero Marks: Negative Marks: -1 In all other cases.

- 1. The number of species among the following which have fractional bond order is \_\_\_\_\_ Li<sub>2</sub>, He<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>2-</sup>, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>2-</sup>, O<sub>2</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, C<sub>6</sub>H<sub>6</sub>, O<sub>3</sub>
- 2. A bcc lattice is made up of hollow spheres of B. Spheres of solid *A* are present in hollow spheres of *B*.

The radius of *A* is half of the radius of *B*. The ratio of total volume of spheres of *B* unoccupied by *A* in a unit cell and volume of unit cell is  $x \times \frac{\pi\sqrt{3}}{64}$ . Find

the value of x.  $Cl_2, hv \rightarrow C_5H_{11}Cl$  (N number of isomeric products)

 $\frac{\text{Fractional}}{\text{distillation}}$  (*M* number of isomeric products)

N and M are respectively value of (N - M) is \_\_\_\_\_.

The total number of carboxylic acid groups in the product *P* is \_\_\_\_\_.

$$O \longrightarrow O$$

$$O \longrightarrow D$$

$$O \longrightarrow$$

 $CH_3$ 

- 5. Two cyclic dienes *A* and *B* have molecular formula C<sub>6</sub>H<sub>8</sub>. The mixture of the two on reductive ozonolysis gave the following products: succinaldehyde, propan-1,3-dial and glyoxal. Mixture of *A* and *B* on hydrogenation produces only cyclohexane. The total sum of the positions of the double bonds in compounds *A* and *B* is \_\_\_\_\_.
- 6. On electrolysis, an alcoholic solution of sodium chloride gives a sweet smelling liquid (*A*) which gives carbylamine reaction and condenses with acetone to form a hypnotic. The number of halogens in (*A*) are \_\_\_\_\_.

#### Section 2 (Maximum Marks: 24)

- This section contains SIX (06) questions.
- Each question has FOUR options. ONE OR MORE THAN ONE of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each will be evaluated according to the following marking scheme:

Full Marks: +4 If only (all) the correct option(s) is (are) chosen;

Partial Marks: +3 If all the four options are correct

but ONLY three options are chosen:

chosen;
Partial Marks: +2 If three

+2 If three or more options are correct but ONLY two options are chosen, and both of which

are correct;

Partial Marks: +1 If two or more options are

correct but ONLY one option is chosen and it is a correct option;

Zero Marks: 0 If none of the options is chosen (i.e., the question is

unanswered);

Negative Marks: -2 In all other cases.

- 7. Which of the following statements is/are correct?
  - (a) Be(OH)<sub>2</sub> is stronger base than Ba(OH)<sub>2</sub>.
  - (b) Be(OH)<sub>2</sub> is more soluble in water than Ba(OH)<sub>2</sub>.
  - (c) Hydroxides of alkali metals are stronger bases than the hydroxides of alkaline earth metals.
  - (d) CsOH is stronger base than KOH.
- 8. Esterification of acetic anhydride by ethanol takes place as

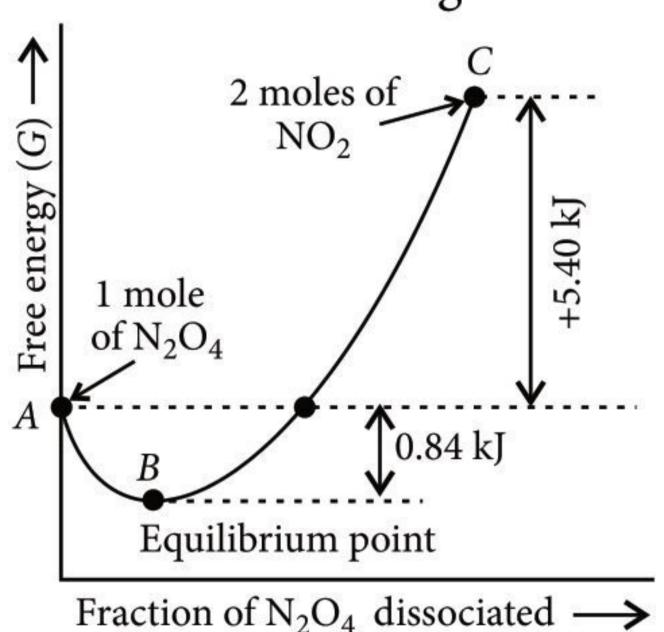
$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

Select the correct statements of the following.

(a) When reaction is carried out in dilute hexane solution, the rate law is given by *k* [Anhydride] [Alcohol].

- (b) When ethanol is the solvent, the rate law is given by k[Anhydride].
- (c) The value of k in the two cases are same.
- (d) Using ethanol as the solvent, its concentration changes significantly during the course of the reaction.
- 9. The compound 'X' with molecular formula  $C_4H_{11}N$  on treatment with  $HNO_2$  gives a tertiary alcohol with molecular formula  $C_4H_{10}O$ . The compound 'X' will give
  - (a) carbylamine reaction
  - (b) Hofmann mustard oil reaction
  - (c) diazonium salt as intermediate with HNO<sub>2</sub>
  - (d) gives 2-methyl-2-nitropropane on oxidation with KMnO₄.
- 10. For the dissociation equilibrium,

 $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ , the variation of free energy with the fraction of  $N_2O_4$  dissociated under standard conditions is shown in the figure :



Which of the following statements are correct?

- (a) The free energy change for the forward reaction is negative.
- (b) The free energy change for the backward reaction is negative.
- (c) The net free energy change for the complete reaction is positive.
- (d) Forward reaction is more spontaneous than backward reaction.
- 11. Which of the following reactions are correctly interpreted?

(a) 
$$Br \longrightarrow Br + CH_3ONa \longrightarrow H_3CO \longrightarrow Br$$

(b) 
$$\longrightarrow$$
 + Ag<sup>+</sup>  $\longrightarrow$  CH<sub>3</sub>OH OCH<sub>3</sub>

(c) 
$$CH_3$$
— $CH$ — $CH_2$ 

$$(d) \xrightarrow{O}_{CHO}_{CHO} \xrightarrow{O}_{OH} \xrightarrow{O}_{OH} \xrightarrow{O}_{OH}$$

12. Me 
$$\xrightarrow{\text{Me}}$$
  $\xrightarrow{\text{HNO}_2}$   $(B)$   $\xrightarrow{RCO_3H}$   $(C)$   $\xrightarrow{\text{LAH}}$   $(D)$   $(A)$ 

(a) (B) is 
$$Me$$

(b) (C) is a cyclic ester

- (c) (D) contains two -OH groups
- (d) (C) is lactone

#### Section 3 (Maximum Marks: 24)

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- Answer to each question will be evaluated according to the following marking scheme:

Full Marks: +4 If ONLY the correct numerical value is entered;

Zero Marks: 0 In all other cases.

13. A compound exists in the gaseous state both as monomer (A) and dimer  $(A_2)$ . The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 L and heated to 273°C. Calculate the

- pressure (in atm) developed, if the compound exists as a dimer to the extent of 50% by weight under these conditions.
- 14. The nucleidic ratio,  ${}_{1}^{3}$ H to  ${}_{1}^{1}$ H in a sample of water is  $8.0 \times 10^{-18}$ : 1. Tritium undergoes decay with a half-life period of 12.3 years. Tritium atoms in 10.0 g of such a sample 40 years after the original sample is collected is  $x \times 10^{5}$ . The value of x is \_\_\_\_\_.
- 15. In transforming 0.01 mole of PbS to PbSO $_4$  the volume of '10 volume'  $H_2O_2$  required will be .
- **16.** The standard reduction potential for  $Cu^{2+}/Cu$  is +0.34 V. What is the reduction potential (in V) at pH = 14 for the above couple? (Given :  $K_{sp}$  of  $Cu(OH)_2 = 1.0 \times 10^{-19}$ ).
- 17. Ferrochrome, an iron-chromium alloy used in making stainless steel, is produced by reducing chromite (FeCr<sub>2</sub>O<sub>4</sub>) with coke:

$$FeCr_2O_{4(s)} + 4C_{(s)} \longrightarrow \underbrace{Fe_{(s)} + 2Cr_{(s)}}_{Ferrochrome} + 4CO_{(g)}$$

The mass of chromium that can be obtained by the reaction of 236 kg of chromite with an excess of coke is (100.57 + x) kg. The value of x is \_\_\_\_\_.

18. An alkyl halide R—X gives nucleophilic substitution reaction with aqueous NaOH. The overall reaction rate in 0.01 M NaOH solution is given by the equation.  $r = 2 \times 10^{-5} [R - X][-OH] + 3 \times 10^{-7} [R - X]$  If the percentage yield of  $S_N 2$  reaction is represented as  $(n \times 10)$  the value of n is \_\_\_\_\_.

#### SOLUTIONS

#### PAPER - I

1. (c): In the reaction sequence of option (c), the end product is a 3°-nitro compound  $(CH_3)_3CNO_2$ . This compound does not have  $\alpha$ -hydrogen and hence, tautomerism is not possible.

2. (c): 
$$XeF_6 + 3H_2O \xrightarrow{Complete} XeO_3 + 6HF$$
 $YeO_6^{4-} + Xe_{(g)} \leftarrow \xrightarrow{Slow disproportionation} HXeO_4^{-} + H_2O + O_{2(g)}$ 

2. (c):  $XeF_6 + 3H_2O \xrightarrow{Complete} XeO_3 + 6HF$ 
 $YeO_6^{4-} + Xe_{(g)} \leftarrow \xrightarrow{Slow disproportionation} HXeO_4^{-} + H_2O + O_{2(g)}$ 

3. (c): From the expression,  $-\Delta T_f = K_f m$ , we get  $m = \frac{-\Delta T_f}{K_f} = \frac{(278.4 - 277.4)}{5.0} = 0.2 \text{ mol kg}^{-1}$ . i.e.,  $C = 0.2 \text{ mol dm}^{-3} \Rightarrow$  (: molality = molarity) given

Now 
$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{(w_1 / M_1)} = \frac{n_2}{w_1} (M_1) = m_0 M_1.$$

or,  $m_0 = \frac{x_2}{M_1} = \frac{0.02}{78 \times 10^{-3}} = 0.257 \text{ mol kg}^{-1}.$ 

i.e.,  $C_0 = 0.257 \text{ mol dm}^{-3}.$ 

Now for the equilibrium reaction,
$$2\text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2$$

$$C_0 - 2x \qquad x$$
we get,  $C = C_0 - 2x$ 
i.e.,  $0.2 \text{ M} = 0.257 \text{ M} - x \text{ or } x = 0.057 \text{ M}.$ 

Thus,  $K_c = \frac{[(\text{CH}_3\text{COOH})_2]}{[\text{CH}_3\text{COOH}]^2} = \frac{x}{(C_0 - 2x)^2}$ 

$$= \frac{0.057}{(0.257 - 2 \times 0.057)^2} = 2.794 \text{ M}^{-1}$$

6. (d): 
$$CH_3CH_2C \equiv CH \xrightarrow{1. NH_2^-} C_2H_5C \equiv CC_2H_5$$

$$C_2H_5 \qquad \qquad \downarrow CP_2C \text{ catalyst})$$

$$H \longrightarrow OH \xrightarrow{COH_4/OH^-} C_2H_5 \qquad \qquad \downarrow CP_2C \text{ catalyst})$$

$$C_2H_5 \qquad \qquad \downarrow CP_2C \text{ catalyst})$$

$$C_2H_5 \qquad \qquad \downarrow CP_5C \equiv CC_2H_5$$

$$C_2H_5 \qquad \qquad \downarrow CP_5C \equiv CC_5C \qquad \downarrow CP_5$$

$$C_2H_5 \qquad \qquad \downarrow CP_5C \qquad \downarrow CP_5$$

$$C_2H_5 \qquad \qquad \downarrow CP_5$$

$$C_2H$$

7. (a,b,c): Magnetic moment,  $\mu = \sqrt{n(n+2)}$  B.M. where, n = No. of unpaired electrons

For X and Z: 
$$\sqrt{n(n+2)} = 3.87$$
 B.M.  
 $n^2 + 2n - 15 = 0 \implies n^2 + 5n - 3n - 15 = 0$   
 $\therefore n = 3$ 

For complex  $Y(1:3 \text{ electrolyte}): \sqrt{n(n+2)} = 0 \Rightarrow n = 0$  $CoCl_2 \cdot 6H_2O$  or  $[Co(H_2O)_6]Cl_2(X)$  is pink coloured compound.

Adding excess of HCl at room temperature, changes (X)into  $[CoCl_4]^{2-}(Z)$  and on adding excess of NH<sub>3</sub> and  $NH_4Cl$  in the presence of air forms  $[Co(NH_3)_6]Cl_3(Y)$ .  $[Co(H_2O)_6]Cl_2 \rightleftharpoons [Co(NH_3)_6]Cl_3$ 

$$(X) (Pink) \qquad (Y)$$

$$(m = 3.87 \text{ B.M})$$
  $(m = 0)$ 

HCl (excess) ↓room temperature

 $[CoCl_4]^{2-}$ 

(*Z*) (Blue)

 $(\mu = 3.87 \text{ B.M.})$ 

$$[\text{Co(NH}_3)_6]\text{Cl}_3 \rightleftharpoons [\text{Co(NH}_3)_6]^{3+} + 3\text{Cl}^{-}$$
(Y)

Thus, it is a 1:3 electrolyte. The hybridisation of Co in  $[Co(NH_3)_6]Cl_3$  is  $d^2sp^3$  (octahedral).

Adding of AgNO<sub>3</sub> to  $[Co(NH_3)_6]Cl_3$  (Y) gives three equivalents of AgCl.

Complex  $Z[CoCl_4]^{2-}$  has  $sp^3$  hybridisation. Thus, it is a tetrahedral complex.

$$[\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^-; \Delta H = -\text{ve}$$
 (c) (i)  $4p_x$  (Blue) (Pink) (Exothermic reaction) (d) (i)  $3d_{x^2}$ 

When ice is added to the solution (0° C), the equilibrium shifts towards right hence, pink colour will remain predominant.

8. (b,c,d): (a) 
$$(CH_3)_3C - CH = CH_2 + Hg(OAc)_2$$
  
 $OH$   
 $NaBH_4 > (H_3C)_3C - CH - CH_3$ 

(b) 
$$C_6H_5 - C - C - C_6H_5 - Ag^+ \rightarrow C_6H_5 - C - C_6H_$$

$$CH_{3} - C - C - C_{6}H_{5} \leftarrow CH_{3} - CH_{3} - CH_{3} - CH_{5} \leftarrow CH_{3} - CH_{5} - CH_{5}$$

(c) 
$$\bigcirc$$
 OH + TsCl  $\longrightarrow$   $\bigcirc$  OTs  $\bigcirc$  CH<sub>3</sub>CH<sub>2</sub>SH  $\bigcirc$  SCH<sub>2</sub>CH<sub>3</sub>

(d) 
$$O = \underbrace{ - H_2/Pt}_{HO} - OH$$

9. (a,b,c)

10. (c, d):  $Br_2/CCl_4$  can be used, allyl bromide being unsaturated will discharge its colour while n-propyl bromide does not. On shaking with aq. AgNO<sub>3</sub>, allyl bromide being more reactive will give pale yellow ppt. of AgBr but *n*-propyl bromide will not.

On boiling with aq. KOH, both will undergo hydrolysis, hence give ppt. of AgBr. Fusion with sodium also converts the bromine of both the compounds into NaBr, thus both give ppt. with AgNO<sub>3</sub>. Hence, reagents given in option (c) and (d) cannot be used to distinguish between allyl bromide and *n*-propyl bromide.

11. (a, b, d): (a) Electron withdrawing groups favour nucleophilic addition.

- (b) Good leaving group favour the process.
- (c) Smaller acids are more reactive.
- (d) Small alkyl groups in ester favour hydrolysis.

12. (a,d): The orbitals of same energy are called degenerate orbitals.

- (a) (i)  $3d_{xy}$
- (ii)  $3d_{yz}$
- (b) (i)  $3p_x$
- (ii)  $3d_{xy}$
- (ii)  $3d_{xy}$
- (d) (i)  $3d_{x^2-v^2}$  (ii)  $3d_{x^2-v^2}$

 $3d_{xy}$  and  $3d_{yz}$ ;  $3d_{x^2-y^2}$  and  $3d_{x^2-y^2}$  represent pair of degenerate orbitals.

13. (0.98): 
$$MBr_{2(aq)} \rightarrow M^{2+} + 2Br^{-}$$
  
 $MBr_{2} + H_{2}S \rightarrow MS + 2HBr$   
 $K_{sp}$  of  $MS = [M^{2+}][S^{2-}]$   
 $6 \times 10^{-21} = [0.05][S^{2-}]$ 

$$\therefore$$
 [S<sup>2-</sup>] = 1.2 × 10<sup>-19</sup> M

Therefore, MS will be precipitated if  $H_2S$  provides  $1.2 \times 10^{-19}$  M ions of  $S^{2-}$ .

Now for H<sub>2</sub>S, H<sub>2</sub>S  $\stackrel{K_1}{\Longrightarrow}$  H<sup>+</sup> + HS<sup>-</sup>  $\stackrel{K_2}{\Longrightarrow}$  2H<sup>+</sup> + S<sup>2-</sup>

$$K = K_1 \times K_2 = \frac{[H^+]^2 [S^{2-}]}{[H_2 S]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[H^+]^2 [1.2 \times 10^{-19}]}{[0.1]}$$

$$\therefore [H^+] = 1.04 \times 10^{-1}$$

$$pH = -\log [H^+] = -[\log (1.04 \times 10^{-1})] = 0.98$$

#### 14. (0.08)

15. (-48.18): Given  $E_1 = 0.6915$  V,  $T_1 = 273$  K  $E_2 = 0.6573$  V,  $T_2 = 298$  K Now  $\Delta G^{\circ} = -nFE^{\circ}$  cell

$$= -2 \times 96500 \times 0.6573 = -126858.9$$

$$\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_{D}$$

where 
$$\frac{\partial E}{\partial T}$$
 = Temperature coeffecient of emf =  $\frac{E_2 - E_1}{T_2 - T_1}$  1. (7): Li<sub>2</sub> = 1, He<sub>2</sub><sup>+</sup> =  $\frac{1}{2}$ , N<sub>2</sub><sup>+</sup> =  $2\frac{1}{2}$ , N<sub>2</sub><sup>2-</sup> = 2,

16. (14): 
$$C \leftarrow CH_3 + H \rightarrow C - H \frac{OH^{-}/\Delta}{(Cross aldol condensation)}$$

 $CH_3$ 

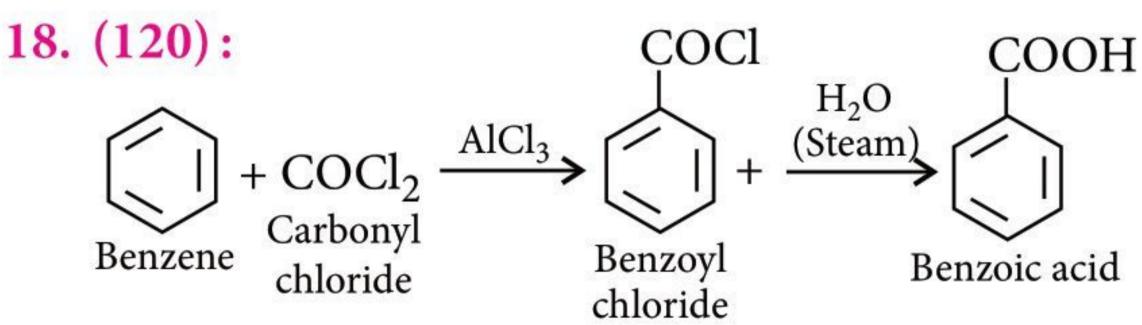
$$\begin{array}{c|c} OH^{-}/\Delta & H-C-H+ \\\hline & (Cross \\ Cannizzaro \\ reaction) \\ OH & CH_3 \\ CH-C-CH_3 + HCOONa \\ \hline & CH_2OH \\ \hline & (Acetal formation takes place) \\ \end{array}$$

17. (1.01): For isothermal expansion,  $\Delta U = 0$ As pressure is constant therefore, process is irreversible.

$$\Rightarrow q_{irrev} = -w_{irrev} = -(-P\Delta V) = -[-3(2 - 1)]$$

$$= 3 \text{ L atm} = 3 \times 101.3 \text{ J}$$

$$\Delta S_{surr} = \frac{-q_{irrev}}{T} = -\frac{3 \times 101.3 \text{ J}}{300 \text{ K}} = -1.013 \text{ J K}^{-1}$$



$$CH_{2}CHCH_{3}$$

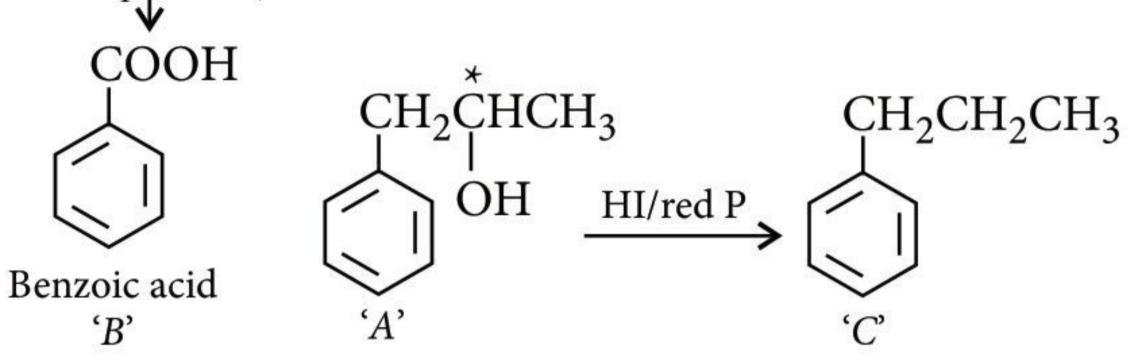
$$CH_{2}COONa$$

$$I_{2}/NaOH$$

$$-CHI_{3}$$

$$CH_{2}COONa$$

(Optically active 'A') KMnO<sub>4</sub> KOH, heat



Molecular weight of 'C' ( $C_6H_5CH_2CH_2CH_3$ ) is  $12 \times 9 + 12 = 108 + 12 = 120 \text{ g mol}^{-1}$ .

#### PAPER - II

1. (7): 
$$\text{Li}_2 = 1$$
,  $\text{He}_2^+ = \frac{1}{2}$ ,  $\text{N}_2^+ = 2\frac{1}{2}$ ,  $\text{N}_2^{2-} = 2$ ,  $\text{O}_2^+ = 2.5, \text{O}_2^{2-} = 1.0, \text{O}_2^- = 1.5, \text{CO}_3^{2-} = 1.33$ ,  $\text{C}_6\text{H}_6 = 1.5, \text{O}_3 = 1.5$ 

2. (7): Let radius of hollow sphere B be r.

:. Edge length 
$$(a) = 4r / \sqrt{3}$$
  
Volume of unit cell =  $a^3 = (4r / \sqrt{3})^3$ 

Volume of *B* unoccupied by *A* (having radius = r/2)

in unit cell = 
$$2 \times \left[ \frac{4}{3} \pi r^3 - \frac{4}{3} \pi \left( \frac{r}{2} \right)^3 \right]$$

 $\therefore$  Volume of B unoccupied by A in unit cell Volume of unit cell

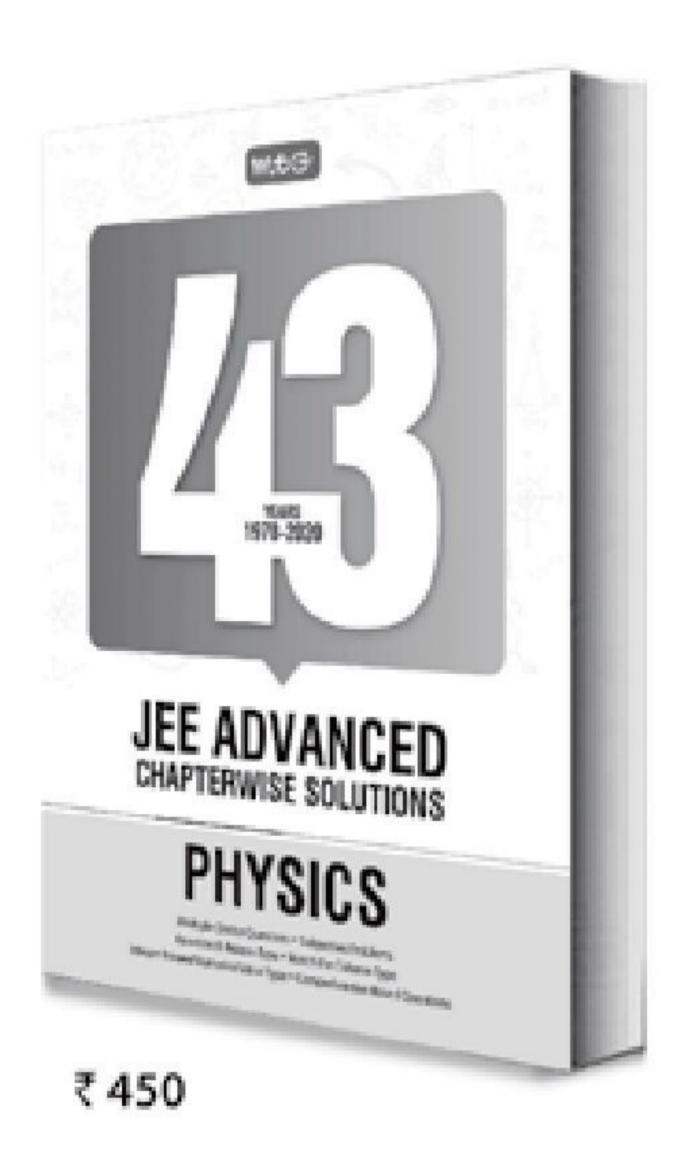
$$=\frac{\frac{4}{3}\pi \times \frac{7r^3}{8} \times 2}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{7\pi\sqrt{3}}{64}$$

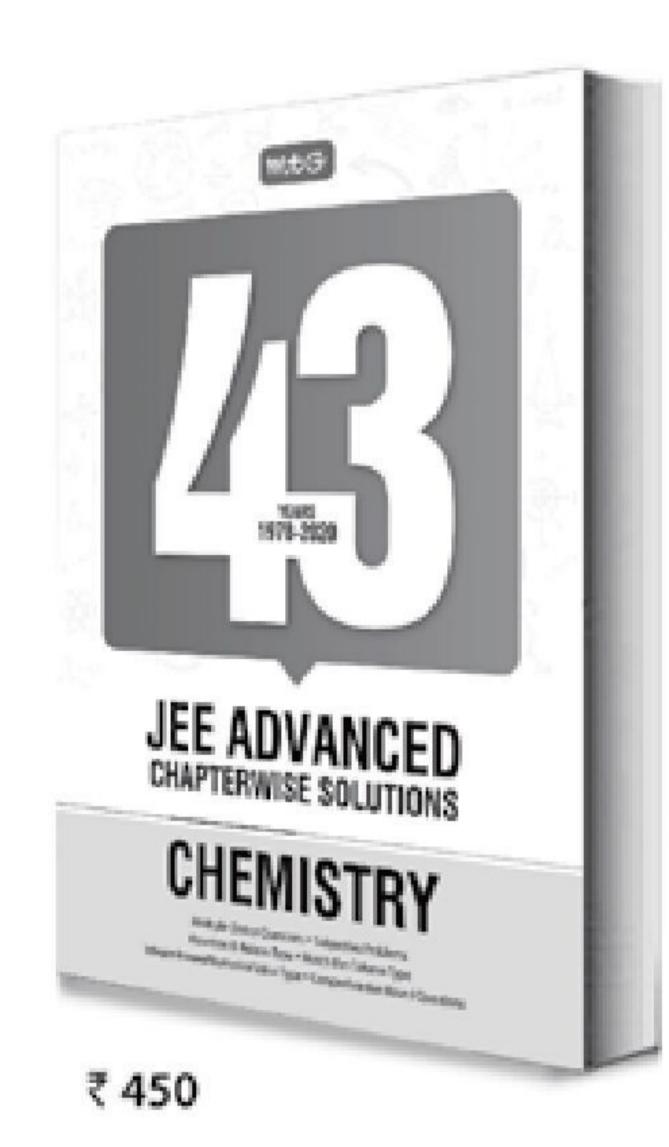
$$\therefore \quad x \times \frac{\pi\sqrt{3}}{64} = \frac{7\pi\sqrt{3}}{64} \quad \therefore \quad x = 7$$

3. (2): In fractional distillation, optical isomers are not separated.



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4. (2):
$$O \xrightarrow{H_3O^+} COOH$$

$$O \xrightarrow{O} O \xrightarrow{O} COOH$$

$$O \xrightarrow{O} O \xrightarrow{O} O \xrightarrow{O} COOH$$

$$O \xrightarrow{O} O \xrightarrow{O} O \xrightarrow{O} O \xrightarrow{O} O$$

$$O \xrightarrow{O} O O$$

$$O \xrightarrow{O} O$$

$$O \xrightarrow{O$$

No. of – COOH groups in the product 'P' is 2.

**5. (9)**: Mixture of *A* and *B* gives cyclohexane on hydrogenation. This implies that both *A* and *B* should be cyclohexadienes. The ozonolysis products suggest the presence of double bonds at 1 and 3-positions on one and at 1 and 4-positions in the other. Hence, *A* and *B* should be

(Cyclohexa-1,3-diene) (Cyclohexa-1,4-diene) (A) (B)

$$(A) \qquad (B) \qquad (B)$$

$$(A) \qquad (B) \qquad (CH_2-CHO \qquad CHO \qquad + | CHO \qquad C$$

Total sum of the positions of the double bonds in A and B = 1 + 3 + 1 + 4 = 9.

6. (3): NaCl 
$$\rightleftharpoons$$
 Na<sup>+</sup> + Cl<sup>-</sup>

At anode Cl<sub>2</sub> is discharged and electrolytic solution contains NaOH on electrolysis. Cl<sub>2</sub> oxidises alcohol to acetaldehyde which is chlorinated to chloral. Chloral on hydrolysis yields chloroform.

$$C_2H_5OH \xrightarrow{Cl_2} CH_3CHO \xrightarrow{Cl_2} CCl_3CHO$$

$$\xrightarrow{NaOH} CHCl_3 + HCOONa$$
(A)

CHCl<sub>3</sub> gives carbylamine reaction and condenses with acetone to form hypnotic.

7. (c,d): Basic character of hydroxide decreases on moving from left to right in a period. Basic character of hydroxides increases on moving down the group.

8. (a,b): (a) In dilute hexane solution, concentration of both anhydride and ethanol change with the

progress of the reaction and the rate depends upon the concentrations of both the reactants.

(b,d) When solvent (ethanol) is also a reactant, its concentration is so large in comparison to anhydride that it remains practically constant. So, the rate does not depend on [ethanol].

(c) The value of k are not the same in the two cases.

9. (a,b,c,d): Since the compound 'X' with molecular formula  $C_4H_{11}N$  on treatment with  $HNO_2$  gives a tertiary alcohol, therefore, (X) must be a 1° amine and as such it must give carbylamine reaction. It undergoes oxidation with  $KMnO_4$  to give 2-methyl-2-nitropropane and must form diazonium salt as an unstable intermediate during its reaction with  $HNO_2$ .

10. (a,b,c):  $\Delta G^{\circ}$  for conversion of 1 mole of N<sub>2</sub>O<sub>4</sub> into equilibrium mixture (forward reaction)

$$= -0.84$$
 kJ, *i.e.*, -ve

 $\Delta G^{\circ}$  for conversion of 2 moles of NO<sub>2</sub> into equilibrium mixture (backward reaction)

$$= -5.40 + (-0.84) = -6.24$$
 kJ, *i.e.*, -ve

 $\Delta G^{\circ}$  for conversion of 1 mole of N<sub>2</sub>O<sub>4</sub> completely into 2 moles of NO<sub>2</sub> = +5.40 kJ.  $\Delta G^{\circ}$  for complete conversion is positive therefore, complete conversion is not possible. As  $\Delta G^{\circ}$  for backward reaction is more negative than for forward reaction, *i.e.*, formation of N<sub>2</sub>O<sub>4</sub> is more spontaneous.

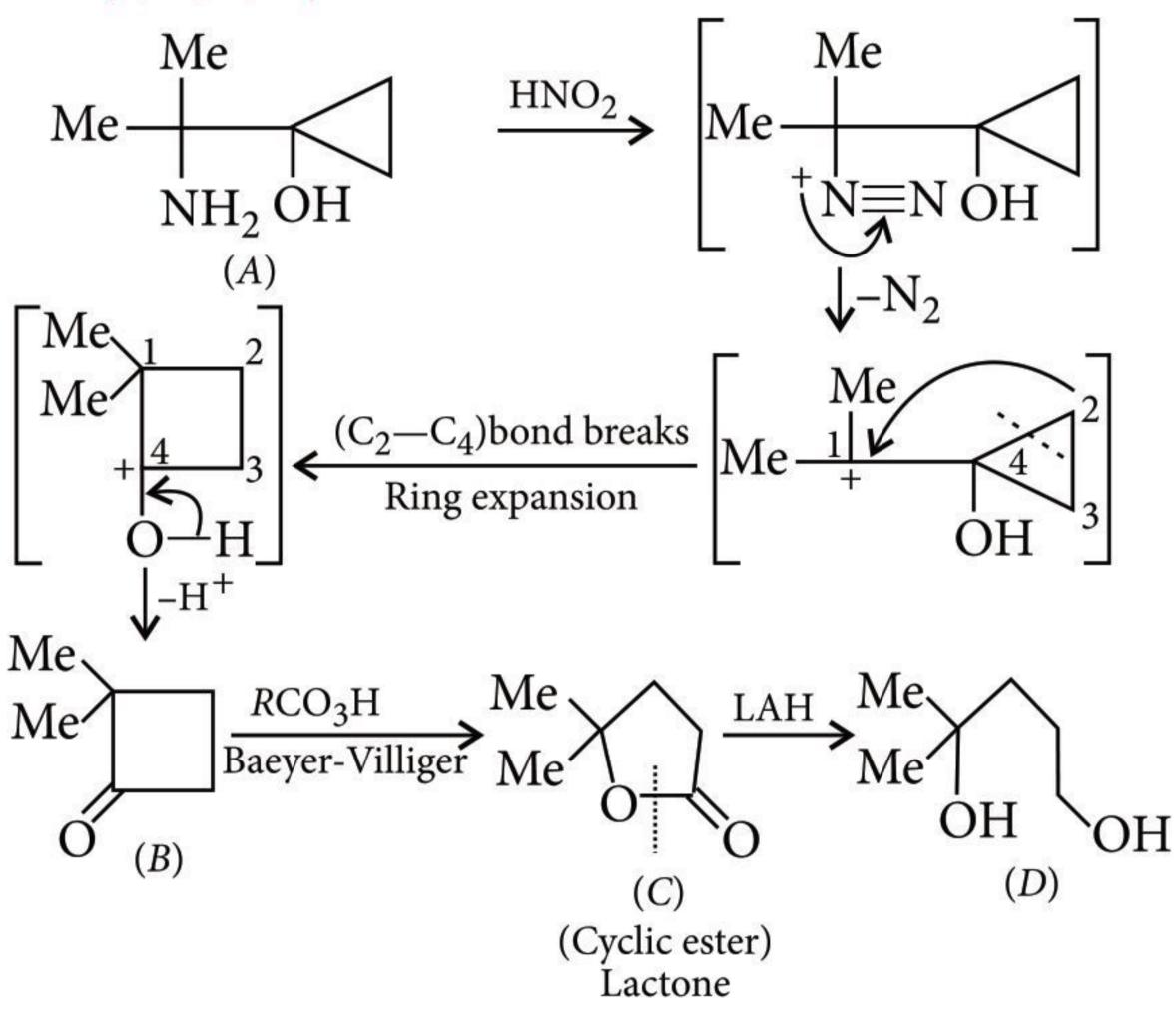
#### 11. (a,b,d):

(a) 
$$Br$$
 $Br$ 
 $Br$ 
 $esonance stable$ 
 $H_3CO$ 
 $Br$ 
 $expansion$ 
 $H_3CO$ 
 $H$ 

$$(d) \bigcup_{H} \bigcup_{O} \bigcup_{H} \bigcup_{O} \bigcup_{Cyclic acetal} \bigcup_{Cyclic acetal}$$

(aldehydes are more reactive than ketones towards Nu- additions.)

#### 12. (a, b, c, d):



13. (2.0): Weight of dimer = 
$$\frac{96 \times 50}{100}$$
 = 48

Number of moles of dimer  $=\frac{48}{96} = 0.5$ 

Number of moles of monomer  $=\frac{48}{48}=1$ 

According to ideal gas equation, PV = nRTor  $P \times 33.6 = 1.5 \times 0.0821 \times 546$ 

or 
$$P = \frac{1.5 \times 0.0821 \times 546}{33.6} = 2.0$$
 atm.

14. (5.62): 18 g  $H_2O$  contains 1  $N_A$  oxygen atoms and 2  $N_A$  hydrogen atoms

Now,  ${}_{1}^{3}H : {}_{1}^{1}H = 8 \times 10^{-18} : 1$ 

18 g H<sub>2</sub>O contains  $8 \times 10^{-18} \times 6.023 \times 10^{23} \times 2$   $^{3}_{1}$ H atoms ∴ 10 g H<sub>2</sub>O contains

 $\frac{10 \text{ g H}_2\text{O contains}}{2.10^{-18}}$ 

$$= \frac{8 \times 10^{-18} \times 6.023 \times 10^{23} \times 2 \times 10}{18} \, {}_{1}^{3} \text{H atoms}$$
$$= 5.35 \times 10^{6} \, {}_{1}^{3} \text{H atoms}$$

Now, 
$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

or 
$$40 = \frac{2.303 \times 12.3}{0.693} \log \frac{5.35 \times 10^6}{N}$$

or  $N = 5.62 \times 10^5$  atoms.

15. (44.8): PbS + 
$$4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$
  
1 mole 4 mole  
0.01 mole 0.04 mole

Weight of 0.04 mole of  $H_2O_2 = 1.36$  g

Now, H<sub>2</sub>O<sub>2</sub> decomposes as:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

 $\Rightarrow$  1mL of 10 volume H<sub>2</sub>O<sub>2</sub> solution contains

$$\frac{68}{22400}$$
 ×10g = 0.03035 g of H<sub>2</sub>O<sub>2</sub>.

 $\Rightarrow 0.03035$  g of  $H_2O_2$  is present in 1 mL of 10 volume  $H_2O_2$ 

∴ 1.36 g of  $H_2O_2$  will be present in

$$\frac{1}{0.03035}$$
 × 1.36 = 44.81 mL of 10 volume H<sub>2</sub>O<sub>2</sub>.

16. (-0.22): For Cu(OH)<sub>2</sub>,  $K_{sp} = [Cu^{2+}] [OH^{-}]^{2}$ 

: 
$$[H^+] = 10^{-14}$$
; thus  $[OH^-] = 10^0 = 1$ 

Therefore, 
$$[Cu^{2+}] = \frac{K_{sp}}{[OH^{-}]^{2}}$$

$$= \frac{1.0 \times 10^{-19}}{1} = 1.0 \times 10^{-19} \text{ M}$$

Now,  $E_{RP}$  for the couple of  $Cu^{2+}/Cu$  is

$$E_{\text{RP}} = E_{\text{RP}}^{\circ} + \frac{0.059}{2} \log_{10} \left[ \text{Cu}^{2+} \right]$$
$$= 0.34 + \frac{0.059}{2} \log_{10} \left[ 1 \times 10^{-19} \right] = -0.22 \text{ V}$$

17. (9): FeCr<sub>2</sub>O<sub>4(s)</sub> + 4C<sub>(s)</sub> 
$$\longrightarrow$$
 Fe<sub>(s)</sub> + 2Cr<sub>(s)</sub> + 4CO<sub>(g)</sub>
1 mol
2 mol
224 g
104 g
112 g

224 kg of chromite gives = 104 kg of Cr

Thus, 236 kg of chromite gives =  $\frac{104 \times 236}{224}$  kg of Cr = 109.57 kg Cr = (100.57 + 9)  $\therefore x = 9$ 

$$OH^- R - OH Rate = k_1[R - X][OH^-]$$
18. (4):  $R - X OH^ S_{N^1} Rate = k_2[R - X]$ 

Overall reaction rate =  $k_1[R-X][OH^-] + k_2[R-X]$ For 0.01 M NaOH solution

$$r = 2 \times 10^{-5} [R - X](0.01) + 3 \times 10^{-7} [R - X]$$
 $S_{N2}$ 

$$r = 2 \times 10^{-7} [R-X] + 3 \times 10^{-7} [R-X]$$

% of S<sub>N</sub>2 reaction = 
$$\frac{2 \times 10^{-7}}{2 \times 10^{-7} + 3 \times 10^{-7}} \times 100$$
$$= \frac{2}{5} \times 100 = 40 = 4 \times 10$$



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\*Arunava Sarkar

#### **Chemistry of Substitution Reactions**

#### **PROBLEMS**

(c)

#### SINGLE OPTION CORRECT

1. Identify the product in the following reaction:

$$\begin{array}{c}
 & \bigcirc \\
 & \bigcirc
\end{array}$$

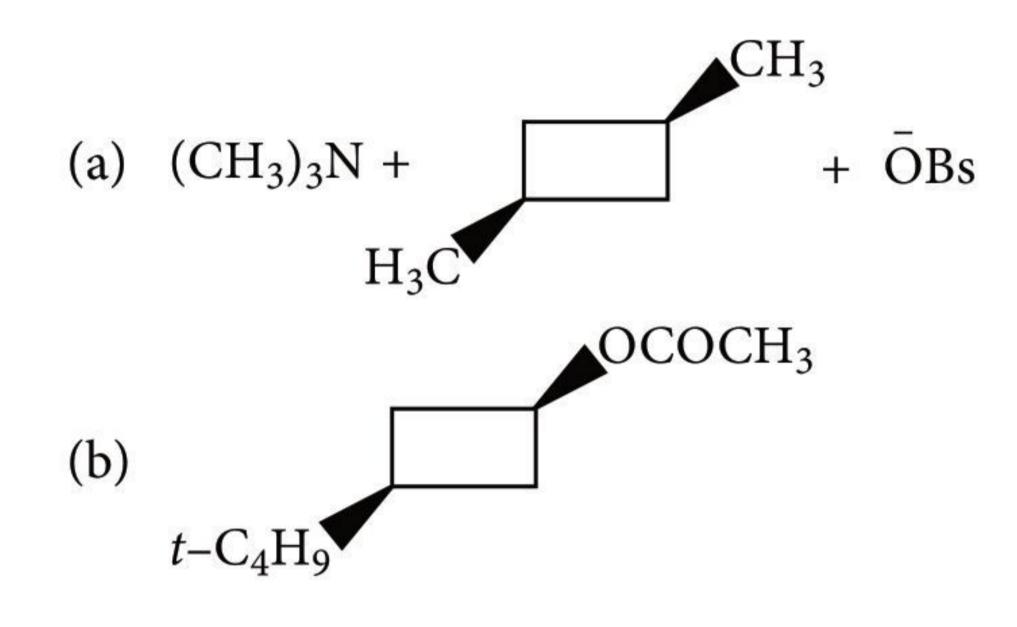
$$\begin{array}{c}
 & \text{aq. NaOH} \\
 & \bigcirc \\
 & \bigcirc
\end{array}$$

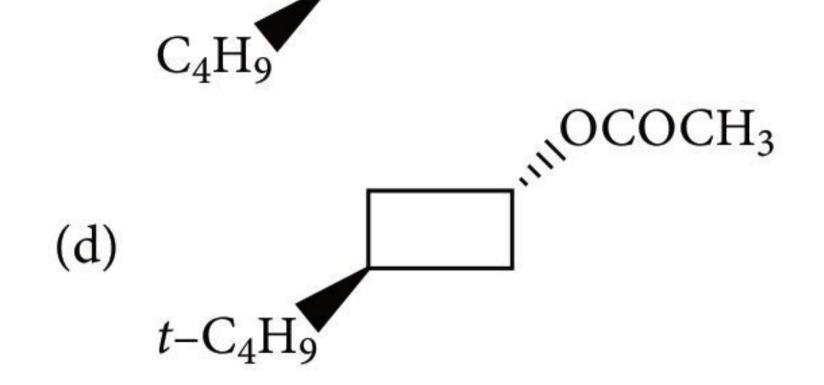
(b) 
$$\frac{Ph}{Ph} > C < \frac{OH}{F}$$

(c) 
$$C - OH$$
 (d) None of these

2. Identify the product:

OBs 
$$CH_3$$
  $CH_3$   $CH_$ 



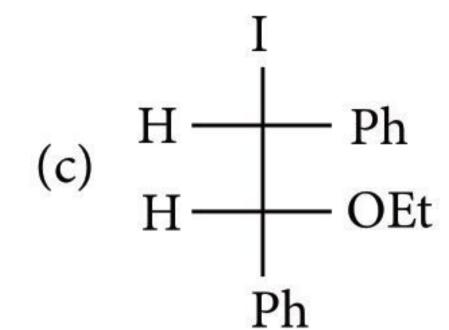


3. EtO

$$H$$
 $H$ 
 $NaI$ 
 $acetone$ 
 $Aceton$ 

(a) 
$$Ph \longrightarrow H$$
 (b)  $H \longrightarrow Ph$   $Ph$   $Ph$   $Ph$ 

\*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna



(d) None of these

4. Arrange the followings according to the increasing order of reactivity in  $S_N$ 2 reaction :

$$(I) \qquad \qquad C1$$

$$(V)$$
 $O$ 
 $Br$ 

- (a) (IV) < (I) < (II) < (III) < (V)
- (b) (II) < (III) < (I) < (IV) < (V)
- (c) (III) < (I) < (II) < (IV) < (V)
- (d) None of these
- 5. The following compound on hydrolysis in aqueous acetone will give

$$P = H_3CO - \left\langle \underline{\phantom{+}} \right\rangle - \frac{Me \quad Me \quad Me}{H \quad OH \quad Me} \left\langle \underline{\phantom{+}} \right\rangle - NO_2$$

$$Q = H_3CO - \left\langle \begin{array}{c} Me & Me \\ \hline \\ OH & H & Me \end{array} \right\rangle - NO_2$$

- (a) a mixture of P and Q
- (b) a mixture of P and R
- (c) a mixture of Q and R
- (d) only R.
- 6. In the following compounds, nucleophile and the leaving groups are in the same molecule:

(II) TfO \

All the species here show dual nature *i.e.*, they can undergo both inter and intra-molecular substitution reaction. For which of the given species intramolecular substitution is most feasible?

- (a) (I), (II)
- (b) (II), (III)
- (c) (III), (IV)
- (d) (IV)
- 7. In the following reaction:

$$\begin{array}{c|c}
Me \\
D \longrightarrow Cl \\
H \longrightarrow Br
\end{array}$$
NaSH (1 eq.)
$$DMSO \longrightarrow Major product$$
Ph

Which option has the correct features for reaction mechanism, leaving group and stereochemistry?

- (a)  $S_N 2/Cl^-/$  inversion
- (b)  $S_N 2/Br^-/inversion$
- (c) S<sub>N</sub>1/Br<sup>-</sup>/racemisation
- (d) E2/Br/anti-elimination
- 8. Which of the following compounds is most rapidly hydrolyzed by  $S_N1$  mechanism?
  - (a)  $C_6H_5Cl$
  - (b)  $Cl-CH_2-CH=CH_2$
  - (c)  $(C_6H_5)_3CC1$
  - (d) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl
- 9. Consider the following substances:

 $I \Rightarrow$  Acetanilide (PhNHCOCH<sub>3</sub>);

 $II \Rightarrow Aniline (PhNH_2);$ 

III  $\Rightarrow$  Benzene (C<sub>6</sub>H<sub>6</sub>);

IV 
$$\Rightarrow$$
 Acetophenone (Ph $-$ C $+$ CH<sub>3</sub>)

The correct order of increasing reactivity towards electrophile  $E^+$  is

- (a) IV < III < II < I
- (b) II < III < IV < I
- (c) I < II < III < IV
- (d) None of these
- 10. Isomeric butyl iodides are:



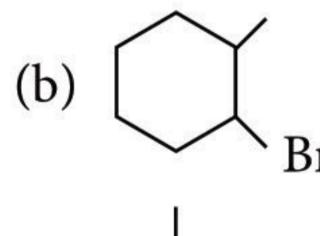
- P.  $(CH_3)_3CI$
- Q. CH<sub>3</sub>CH<sub>2</sub>CHI
- R.  $(CH_3)_2CHCH_2I$
- S. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I

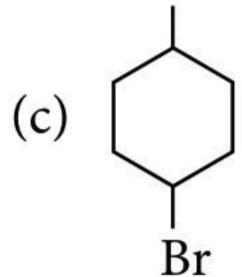
Arrange these according to the increasing order of reactivity in  $S_N$ 2 reaction.

- (a) P < Q < R < S
- (b) P < R < Q < S
- (c) S < R < P < Q
- (d) None of these
- 11. Identify the product in the following reaction.

$$(R \text{ isomer})$$
 CH—Cl  $\stackrel{::}{OH}$  .

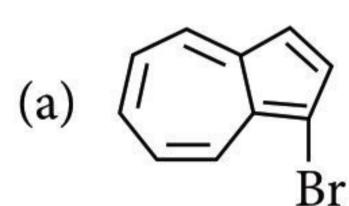
- (a) HO-C CHMe
- (b)  $HO-CEt_2$ CH-OH Me (R)
- (c)  $HO-CEt_2$ CHOH (d) Both (b) and (c) Me (S)
- 12.  $R X + KCN \longrightarrow RCN + KX$ Which of the following solvents will favour this
  - reaction?
  - (a) Ethanol
- (b) Ethyl acetoacetate
- (c) DMSO
- (d) None of these
- 13. In which of the following cases  $S_N1$  and  $S_N2$  products will be same ? (excluding stereoisomers)





14. Identity the product in the following reaction.

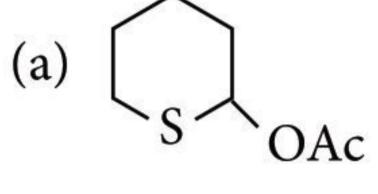
$$\begin{array}{c}
\text{NBS/CH}_2\text{Cl}_2\\
\text{Br}
\end{array}$$

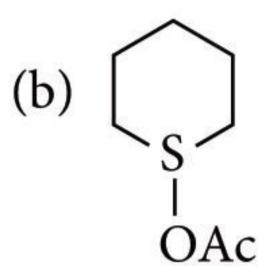


- (c) Both (a) and (b)
- (d) None of these
- 15. Arrange the following nucleophiles as per their decreasing order of nucleophilicity in protic solvent:

- (a)  $\ddot{S}H > Ac\ddot{O} > H_2O > \ddot{O}H > Ph\ddot{O}$
- (b)  $PhO > AcO > H_2O > SH > OH$
- (c)  $\bar{S}H > \bar{O}H > H_2O > Ph\bar{O} > Ac\bar{O}$
- (d) None of these

16. 
$$\underbrace{ \begin{cases} Ac_2O/NaOAc \\ S \end{cases}}_{heat}$$
 Major product = ?





(c) 
$$\left(\begin{array}{c} \\ \\ \\ \end{array}\right)$$
 COO

- (d) None of these
- 17. Arrange the following according to the decreasing order of rate of  $S_N$ 2 reaction :
  - (I)  $CH_3Cl$

(II) 
$$CH_3-C-CH_2-CI$$

- (IV)  $CH_3CH_2-Cl$
- (a) I > II > III > IV
- (b) IV > II > III > I
- (c) II > III > IV > I
- (d) None of these



- 18. Arrange the following in decreasing order of nucleophilicity:
  - $NH_2-NH_2$
- (II) PhNH<sub>2</sub>
- (III) NH<sub>2</sub>
- (IV) NH<sub>3</sub>
- I > III > IV > II
- (b) III > I > IV > II
- II > III > I > IV
- (d) None of these

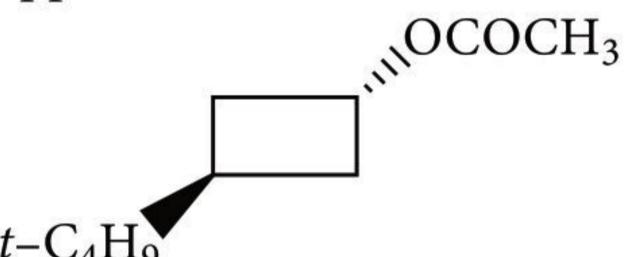
#### **SOLUTIONS**

(c): This is a clear cut substitution reaction.

F, even though a very poor leaving group will leave because of the formation of stable triphenyl methyl carbocation intermediate.

- $\therefore$  Product is (c).
- (d): First of all identify the nucleophile. It is  $-C-CH_3$ . Now, of course here the nature of reaction

is  $S_N$ 2. So, after the brosylate ion leaves (–OBs) product appear to be



- Option (d) is correct.
- (a): First draw the Sawhorse projection of the given Fischer projection.

Option (a) is correct. Even if you go with NGP concept major product will be (a) only.

- 4. (a): Leaving group ability is I > Br > Cl. More branching will decrease the chance of S<sub>N</sub>2 reaction. Presence of a carbonyl group at the adjacent position will increase the possibility of  $S_N$ 2 reactivity. Hence, by considering all the points, (IV) < (I) < (II) < (III) < (V)should be the correct order.
- 5. (a): The given halide is a crowded one. It will definitely undergo S<sub>N</sub>1 reaction. Acetone helps to dissolve the halide. Now, see how the reaction proceeds:

Now, for sure, (I) can undergo a hydride shift to give a more stable carbocation (II).

$$H_3CO$$

Me Me Me Me

 $H_3CO$ 
 $H_3CO$ 

Remember, in (I) methyl shift cannot take place as it will lead to the formation of less stable carbocation.

- .. A mixture of P and Q will be formed.
- Correct option is (a).
- 6. (c): Remember that intramolecular substitution will give a ring structure. The ring that will be more strained (mainly 3 or 4 member) will not be formed. Less strained five and six membered rings will be formed. So, according to this, correct option is (c).

- 7. (b):  $\overline{B}r$  is a better leaving group than  $\overline{C}l$ . DMSO is a polar aprotic solvent which will favour  $S_N2$  reaction. Obviously, inversion will take place.
- :. Correct option is (b).
- 8. (c):  $(C_6H_5)_3\overset{+}{C}$  is most stable carbocation there. So, it will undergo  $S_N1$  reaction most rapidly.

9. (a): 
$$O = C - CH_3$$
  $O = C - CH_3$ 

IV

Deactivating due to +ve charge on carbon. :NH<sub>2</sub>

Highly activating due to +R effect of  $-NH_2$  group.

Some fraction of the electron density does not come to the benzene ring

- ∴ Correct order is IV < III < II < I.
- .. Option (a) is correct.
- 10. (a): With more branching reactivity in  $S_N$ 2 reaction decreases.
- .. Option (a) is correct.
- 11. (b):

- :. Option (b) is correct.
- 12. (c): Among the given solvents, DMSO will favour this reaction.
- 13. (c): Except (c) in all other cases different products are obtained either with rearrangements or any other mean. Option (c) has got a plane of symmetry too.
- :. Correct option is (c).
- 14. (d): Free radical mechanism is involved in this reaction.
- 15. (d): Correct order is

$$\ddot{S}H > \ddot{O}H > Ph\ddot{O} > Ac\ddot{O} > H_2O$$

Anions are stronger nucleophile than neutral molecule. In  $Ac\ddot{O}$  the negative charge is better resonance stabilised than that of  $Ph\ddot{O}$  as  $Ac\ddot{O}$  has equivalent resonance structure.

#### 16. (a):

$$\begin{array}{c}
CH_3-C-O-C-CH_3 \\
CH_3 \\
CO \\
CH_5 \\
C$$

- :. Correct option is (a).
- 17. (d): Rate of  $S_N$ 2 reaction  $\infty$  magnitude of + ve charge  $\infty$   $\frac{1}{\text{Steric crowding}}$
- $\therefore$  Correct order is II > I > IV > III.
- .. Correct option is (d).
- 18. (b): Anion here is  $NH_2$  and hence it will be best nucleophile here. In  $NH_2$ — $NH_2$ , both the nitrogen atoms hold lone pair and a possible repulsion can also work here which in turn increases the donation of lone pair. PhNH<sub>2</sub> will be least as here the lone pair is delocalised. So the order is, III > I > IV > II.
- :. Correct option is (b).



Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit

#### States of Matter: Gases & Liquids | Thermodynamics

States of Matter : Gases & Liquids

#### GASEOUS STATE OF MATTER

#### **Intermolecular Forces**

	Dispersion forces or London forces	Dipole-dipole forces	Dipole-induced dipole forces
1.	Between atoms and non-polar molecules	Between molecules having permanent dipole	Between polar and non-polar molecules
2.	No polarity in the system	Polarity in the system	Induced polarity in non-polar molecules
3.	Atom A Atom B Atom A Atom B A momentary dipole is formed.	δ+ δ- δ+ δ- Electrostatic attraction between the oppositely charged end of different dipoles.	Induced dipole Permanent dipole  Blectron cloud gets deformed due to influence of dipole
4.	Example: Non-polar molecules	Example : HCl	Example : HCl and Ar
	$H_2$ , $N_2$ , $O_2$ , $Cl_2$ , $He$ , $Ne$		

#### **Gas Laws**

Law	Representation	Graphical representation	Applications
Boyle's law states that volume of a given mass of gas is inversely proportional to its pressure at constant temperature.	$V \propto \frac{1}{P}$ $PV = \text{constant}$ (at constant temperature)	$V \uparrow \qquad V \uparrow \qquad V \uparrow \qquad T_2 > T_1$ $\frac{1}{P} \longrightarrow \qquad P \longrightarrow$	Determining volume using equation $P_1V_1 = P_2V_2 =$

Charles' law states that volume of a given mass of gas is directly proportional to the absolute temperature at constant pressure.	$V \propto T$ $\frac{V}{T} = \text{constant}$ (at constant pressure)	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	To calculate volume at different temperatures. $V_t = V_0 \left( 1 + \frac{t^{\circ}C}{273.15} \right)$ $V_0 = \text{volume at 0°C}$
Gay-Lussac's law states that pressure of a given mass of gas is directly proportional to absolute temperature at constant volume.	$P \propto T$ $\frac{P}{T} = \text{constant}$ (at constant volume)	$ \uparrow P V_2 > V_1 V_2 $ $ T \rightarrow $	To calculate pressure at different temperatures. $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

#### Avogadro's Law

- Equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules.
- $V \propto n$  (at constant temperature and pressure) where n = number of moles

#### IDEAL GAS EQUATION

- Combined gas law:  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- Thus,  $\frac{PV}{T} = \text{constant} = K$ ,  $K \propto n$  or K = nRPV/T = nR or PV = nRT
- The gases which obey the ideal gas equation under all conditions of temperature and pressure are called ideal gases.

Units of pressure	Units of volume	Values of gas constant (R)	Units of gas constant (R)
atm	L	0.0821	$L atm K^{-1} mol^{-1}$
atm	cm <sup>3</sup>	82.1	$atm cm^3 K^{-1} mol^{-1}$
dynes cm <sup>-2</sup>	cm <sup>3</sup>	$8.314 \times 10^{7}$	ergs K <sup>-1</sup> mol <sup>-1</sup>
dynes cm <sup>-2</sup>	cm <sup>3</sup>	1.987	$cal K^{-1} mol^{-1}$
Pa or N m <sup>-2</sup>	m <sup>3</sup>	8.314	$J K^{-1} mol^{-1}$

Relationship between molar mass and density:

Let *m* be the mass of a gas in grams and *M* be the molar mass of that gas.

We know,  $n = \frac{m}{M}$ ; Now,  $PV = nRT = \frac{m}{M}RT$ 

$$P = \frac{m}{V} \frac{RT}{M} = \frac{dRT}{M}$$
 or  $M = \frac{dRT}{P}$ 

 $\frac{dT}{P} = \frac{M}{R}$ , since *M* and *R* are constant for a gas.

$$\therefore \frac{dT}{P} = \text{constant} \quad \therefore \quad \frac{d_1T_1}{P_1} = \frac{d_2T_2}{P_2}$$

#### **Dalton's Law of Partial Pressures**

- The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.
- $P_{\text{total}} = p_1 + p_2 + p_3 + ...$   $p_1 = P_{\text{total}} \times \text{mole fraction of gas 1.}$  i.e., partial pressure = total pressure × mole fraction

#### **Graham's Law of Diffusion**

Under similar conditions of temperature and pressure, rates of diffusion of different gases are inversely proportional to the square root of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \text{ or } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

#### KINETIC MOLECULAR THEORY OF GASES

Given by Bernoulli in 1738 and developed by Clausius, Maxwell, Kroning and Boltzmann in 1860. Postulates are:

- The dimensions of the particles are negligibly small compared to the average distance between them.
- The molecules of the gas are in constant random, rapid and chaotic motion. The measured gas pressure is due to the collisions of the gas molecules with the surfaces of containing vessels.
- All collisions are perfectly elastic, and the molecules have no interactions apart from these collisions.
- The average kinetic energy of the molecules is related to the temperature of the gas. The greater the temperature, the greater the kinetic energy.

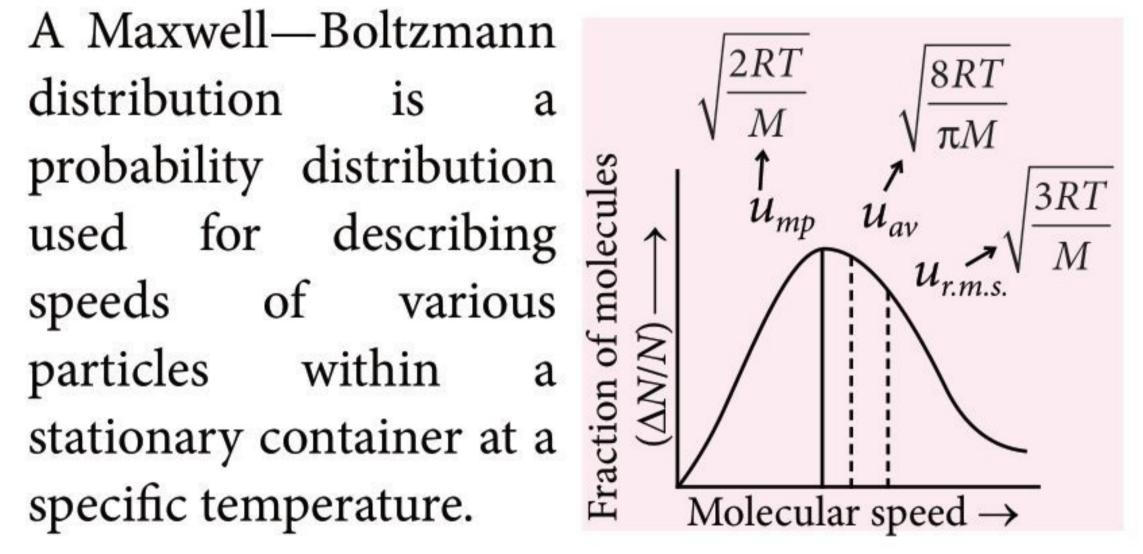
#### Relation among $C_{mp}$ , $C_{av}$ , $C_{rms}$

$$C_{mp}: C_{av}: C_{rms} = \sqrt{\frac{2RT}{M}}: \sqrt{\frac{8RT}{\pi M}}: \sqrt{\frac{3RT}{M}}$$

$$= 1: 1.128: 1.224$$
 $C_{av} = 0.9213 \times C_{rms}, \quad C_{mp} = 0.8165 \times C_{rms}$ 

#### MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

A Maxwell—Boltzmann specific temperature.



#### DEVIATION FROM IDEAL GAS BEHAVIOUR

- Real gases do not follow ideal gas equation perfectly at all conditions of temperatures and pressures.
- $\frac{PV}{nRT} = Z =$ Compressibility factor
  - For an ideal gas, Z = 1
  - For a real gas: Z > 1 (Positive deviation) Z < 1 (Negative deviation)
- Equation of state for real gases (van der Waals'

equation): 
$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

where, a and b are van der Waals' constants.

#### LIQUEFACTION OF GASES

- Gases can be liquefied by decreasing temperature or increasing pressure.
- Critical pressure: The minimum pressure required to liquefy a gas at its critical temperature.

$$P_c = \frac{a}{27b^2}$$

- Critical volume: Volume occupied by one mole of a gas at its critical temperature and pressure.  $V_c = 3b$
- Critical temperature: A temperature above which a gas cannot be liquefied however high pressure may be applied on the gas.

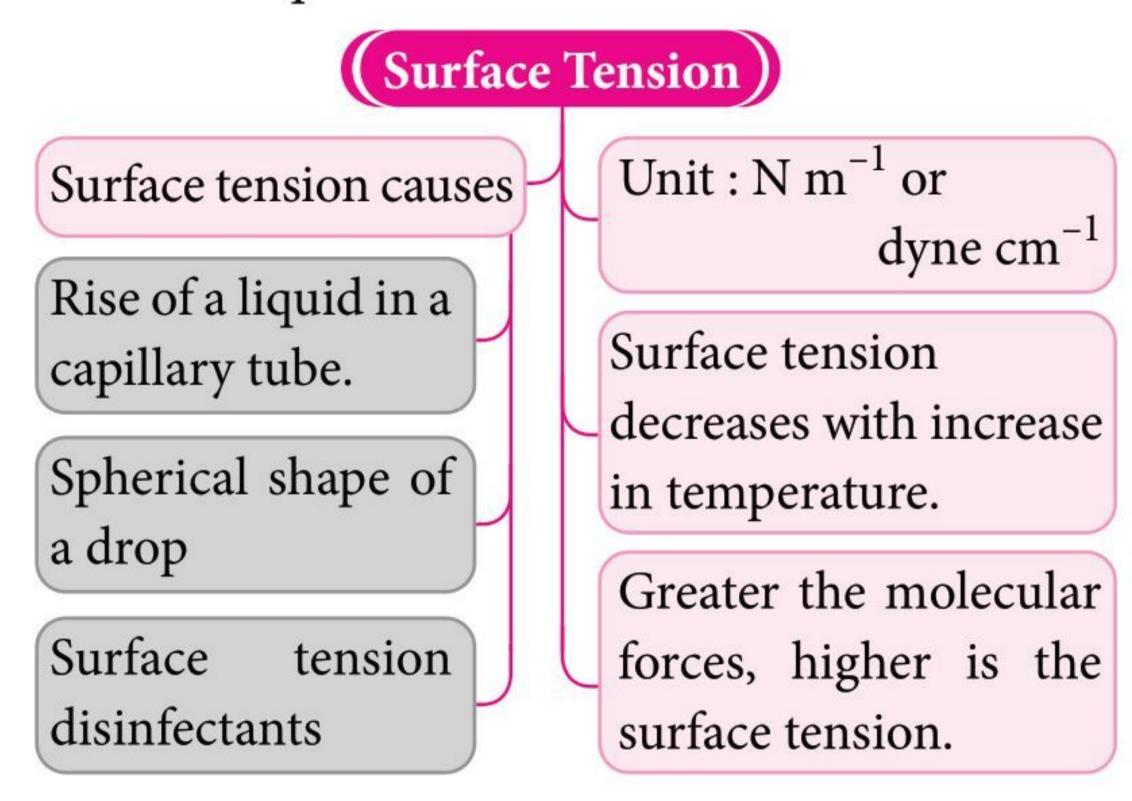
$$T_c = \frac{8a}{27Rh}$$

#### LIQUID STATE OF MATTER

Liquids have definite volumes but not definite shapes.

#### **Properties of Liquid State**

- Boiling point: Temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.
- Surface tension: Force per unit length acting perpendicular to the tangential line drawn at the surface of liquid is known as surface tension.



Viscosity: Internal resistance to the flow in liquids.

$$F = \eta A \frac{dv}{dx}$$
, where,  $A = \text{Area}$ ,  $\frac{dv}{dx} = \text{Velocity gradient}$ ,  $\eta = \text{Coefficient of viscosity}$ ,

#### Thermodynamics

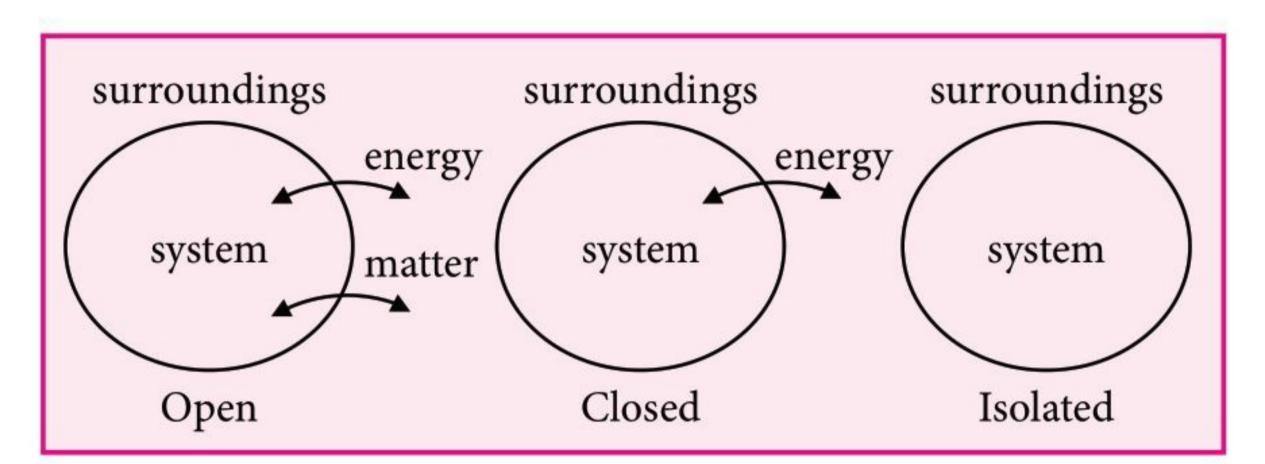
A specified part of the universe which is under thermodynamic consideration is called the system.

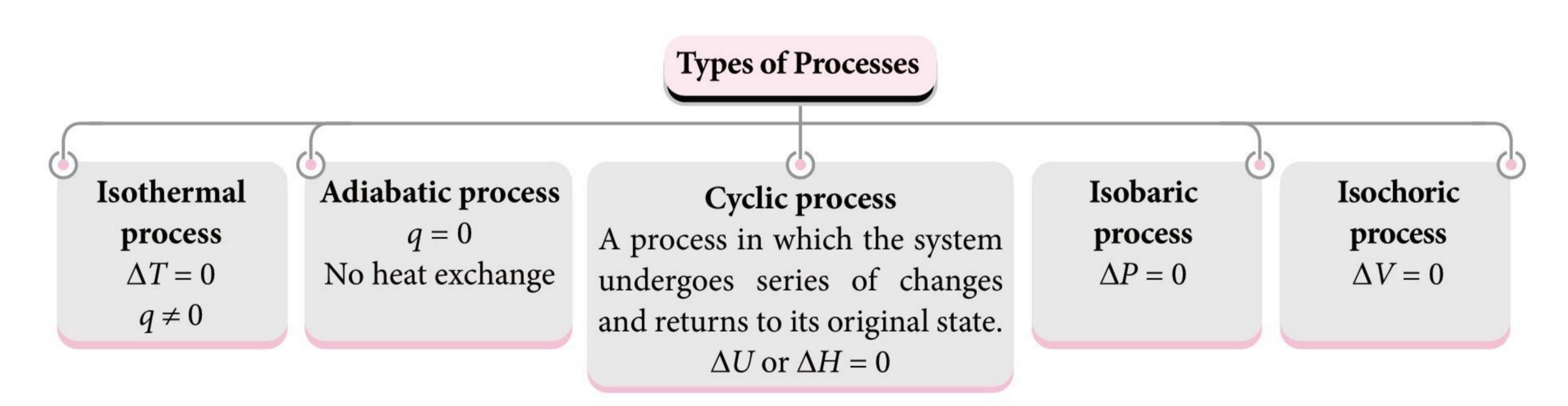
#### THERMODYNAMICS TERMS

- Extensive properties: Properties of the system whose value depends upon the amount or size of the substance present in the system *e.g.*, Gibbs free energy, enthalpy, entropy, internal energy, etc.
- Intensive properties: Properties of the system whose value is independent of the amount or size of the substance present in the system but depends only upon the nature of the substance *e.g.*, temperature, pressure, viscosity, etc.
- State function: A physical quantity is said to be a state function if its value depends only upon the

- state of the system and is independent of the path by which the state is reached *e.g.*, volume, temperature, internal energy, enthalpy.
- Path function: A physical quantity is a path function if it depends upon the path by which the change is brought about *e.g.*, work and heat.

#### **Different Types of Systems**





#### FIRST LAW OF THERMODYNAMICS

Energy can neither be created nor destroyed, although it can be converted to one form to another form. The total energy of the universe remains constant.

$$\Delta U = q + w$$

where,  $\Delta U$  = Change in internal energy;

q = heat change; w = work done

#### **Sign Conventions**

q = +ve (when heat is absorbed by the system)

q = -ve (heat is evolved by the system)

w = +ve (work is done on the system)

w = -ve (work is done by the system)

#### Work

• For isothermal reversible expansion,

$$q = -w = p_{ext} (V_f - V_i)$$

$$= nRT \ln \frac{V_f}{V_i}$$

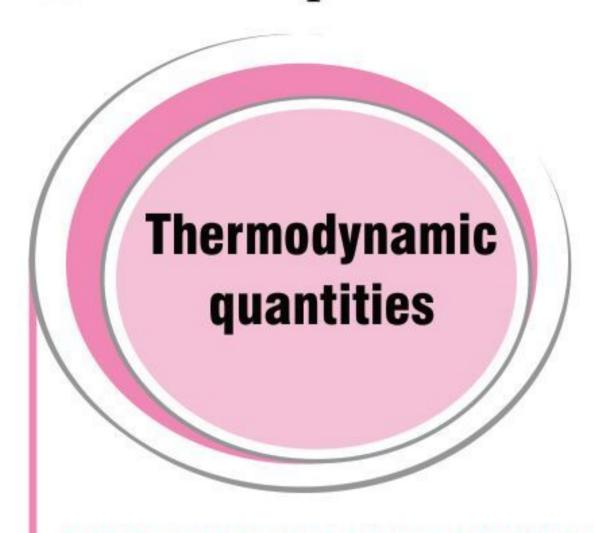
$$= 2.303 \ nRT \log \frac{V_f}{V_i}$$

$$= 2.303nRT \log \frac{P_i}{P_f}$$

• For adiabatic reversible process, q = 0

$$\Delta U = w_{\rm ad} = nC_v \Delta T = \frac{nR}{\gamma - 1} \Delta T$$

Some important thermodynamic quantities:



#### Heat

Heat evolved or absorbed,  $\Delta q = ms\Delta t$ q = +ve (Heat absorbed by the system) m =mass of the substance q = -ve (Heat evolved from the system) M = molecular mass of the substance

#### Internal energy

$$\Delta U = U_2 - U_1$$

$$\Delta U = + \text{ve} (U_2 > U_1)$$

$$\Delta U = -\text{ve} (U_2 < U_1)$$

$$\Delta U = 0$$
 (cyclic process)

 $\Delta U = q_{\nu}$  (at constant volume)

$$\Delta U = Q \times \Delta t \times \frac{M}{m}$$

where Q = heat capacity of the calorimeter,

 $\Delta t$  = rise in temperature

#### Heat capacity

$$C = \frac{q}{\Lambda T}$$

$$C_{\nu} = \left(\frac{dq}{dT}\right)_{\nu} = \left(\frac{\partial U}{\partial T}\right)_{\nu}$$

$$C_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

#### Work

$$w_{\text{irr}} = -P_{\text{ext}} \Delta V$$

$$w_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1}$$

$$= -2.303nRT \log \frac{P_1}{P_1}$$

#### Enthalpy

$$\Delta H = \Delta U + P\Delta V$$
  
 $\Delta H = q_p$  (at constant pressure)

In case of solids and liquids,

$$\Delta H \approx \Delta U \text{ as } P\Delta V \approx 0$$

In case of gases,

$$\Delta H = \Delta U + \Delta n_g RT$$

#### Specific heat capacity

$$C_s = \frac{C}{m} \text{ in JK}^{-1} \text{ g}^{-1}$$

#### Molar heat capacity

$$C_s = \frac{C}{m} \text{ in JK}^{-1} \text{ g}^{-1}$$
  $C_m = \frac{C}{n} \text{ in JK}^{-1} \text{ mol}^{-1}$ 

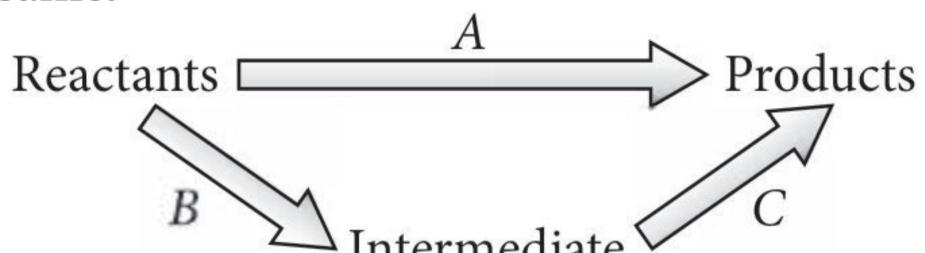
#### Clausius-Clapeyron Equation

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

 $\Delta H_{vap}$  = Molar heat of vaporisation

#### HESS'S LAW

Hess's law states that, if a reaction can take place by more than one route and the initial and final conditions are same, the total enthalpy change is the same.



 $\Delta H_A = \Delta H_B + \Delta H_C$ 

Applications: Heat changes for those reactions can be calculated whose experimental determination is not possible.

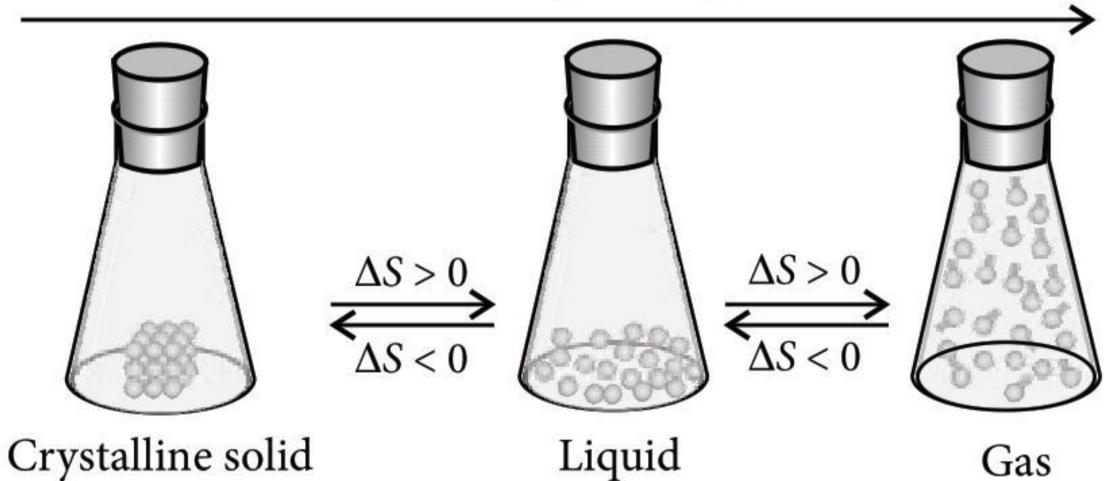


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#### SECOND LAW OF THERMODYNAMICS

Entropy: Measure of degree of disorder or randomness of the system.

Increasing entropy



- $\Delta S = \Sigma S_{\text{(products)}} \Sigma S_{\text{(reactants)}}$
- $\Delta S = \frac{q_{rev}}{T}$
- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- $\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_m}, \ \Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_b}, \ \Delta_{\text{sub}} S = \frac{\Delta_{\text{sub}} H}{T_{\text{sub}}}$

# CONCEPT

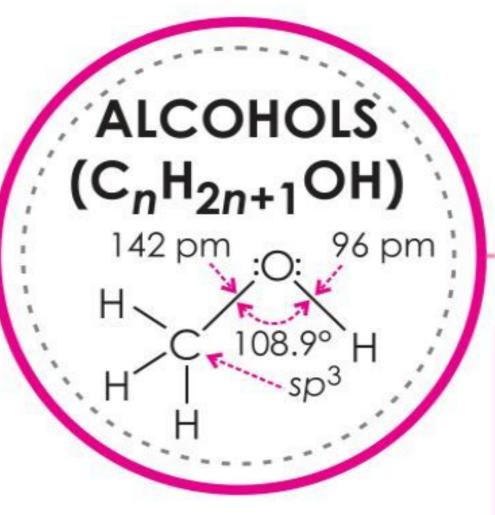
# ALCOHOLS, PHENOLS AND ETHERS

Alcohols, phenols and ethers are the basic compounds of organic chemistry and they find wide applications in industry as well as in day-to-day life.

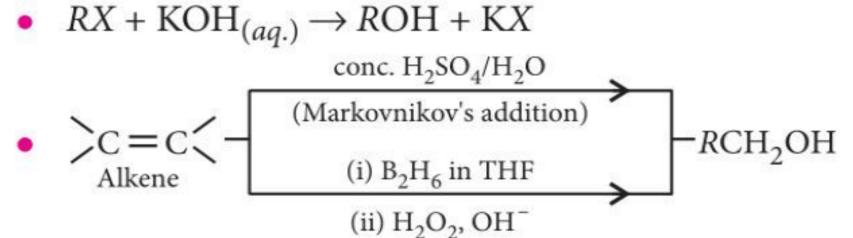


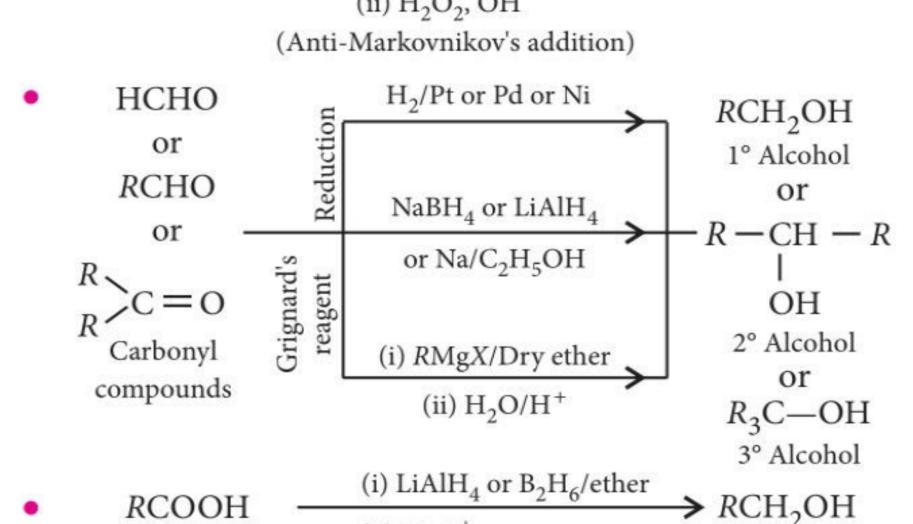
B.pt. 
$$\infty$$
 No. of C-atoms  $\infty$   $\frac{1}{\text{Branching}}$ 

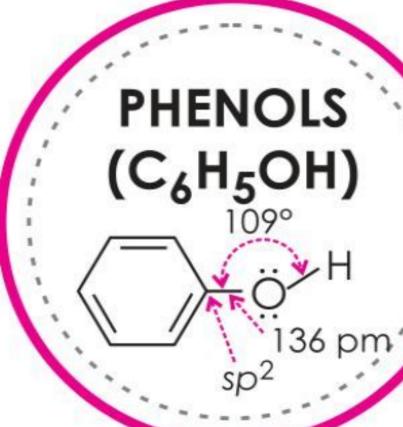
Solubility  $\infty$   $\frac{1}{\text{Size}}$   $\infty$  Branching



#### **Preparation**







#### **Physical properties**

(ii) H<sub>3</sub>O<sup>+</sup>

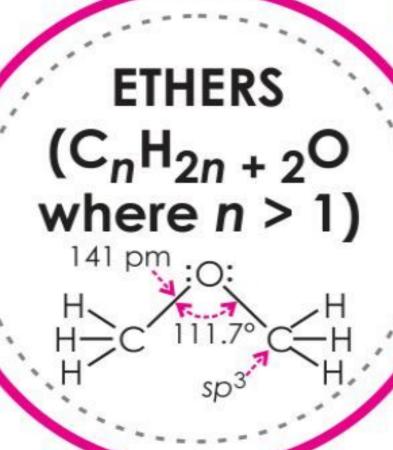
Pure phenols are colourless liquids or solids.

Carboxylic acids

• Form intermolecular hydrogen bonds hence, soluble in water.

#### **Preparation**

$$\begin{array}{c|c} \textbf{C}_{6}\textbf{H}_{5}\textbf{SO}_{3}\textbf{H} & \frac{\textbf{NaOH}}{-\textbf{H}_{2}\textbf{O}} \\ \textbf{C}_{6}\textbf{H}_{5}\textbf{SO}_{3}\textbf{Na} & \frac{\textbf{NaOH}}{573\text{-}623} \text{ K,} \\ \textbf{C}_{6}\textbf{H}_{5}\textbf{ONa} & \frac{\textbf{dil. HCl}}{-\textbf{NaCl}} \\ \textbf{C}_{6}\textbf{H}_{5}\textbf{N}_{2}^{+}\textbf{Cl}^{-} + \textbf{H}_{2}\textbf{O} & \frac{\textbf{dil. H}_{2}\textbf{SO}_{4}, \Delta}{-\textbf{N}_{2}, -\textbf{HCl}} \\ \textbf{C}_{6}\textbf{H}_{5}\textbf{Cl} + \textbf{NaOH} & \frac{623 \text{ K, } 320 \text{ atm}}{-\textbf{NaCl, -H}_{2}\textbf{O}} \\ \textbf{C}_{6}\textbf{H}_{5}\textbf{ONa} & \frac{\textbf{dil. HCl}}{-\textbf{NaCl}} \\ \textbf{O} \\ \textbf{+} \textbf{+} \textbf{HCl} + \frac{1}{2}\textbf{O}_{2} & \frac{\textbf{CuCl}_{2}/\text{FeCl}_{3}}{+\textbf{H}_{2}\textbf{O}} \\ \textbf{(Raschig's process)} \end{array}$$



#### Classification

- Simple or symmetrical: Same alkyl groups are attached to oxygen, ROR.
- Mixed or unsymmetrical: Different alkyl groups are attached to oxygen, ROR'.
- **Aliphatic ethers**: R and R' both are alkyl groups.
- **Aromatic ethers:** Either one or both R and R' are aryl groups.

#### **Chemical properties**

Reaction of ethereal oxygen :

$$ROR + HCl(conc.) \longrightarrow \begin{bmatrix} R > + \\ R > - H \end{bmatrix} CI^-$$

Cleavage of C – O bond :

$$R - OR + HX \xrightarrow{373 \text{ K}} R - OH + R - X$$

- In case of alkyl aryl ethers, phenol and an alkyl halide are obtained.

$$ROR + H_2O \xrightarrow{\text{dil. } H_2SO_4} 2R - OH$$
  
 $ROR + PCl_5 \xrightarrow{\Delta} 2R - Cl$ 

- Reactions involving alkyl group:
- Formation of peroxides with air and light.
- Substitution products obtained on halogenation.
- Electrophilic substitution reactions:

Aryl alkyl ethers give o- and p-substituted products due to +R effect of alkoxy group (-OR).

#### Chemical properties

- Cleavage of O—H bond: Ease of reaction depends on stability of alkoxide ion.
  - Acidity: Phenols > Water > 1° alcohol > 2° alcohol > 3° alcohol
- Cleavage of C—OH bond: Ease of reaction depends on stability of carbocations.

Order of reactivity: 3° alcohol > 2° alcohol > 1° alcohol

• Reactions involving whole alcohol molecule:

Reactions involving whole alcohol molecule:

Dehydration: 
$$R-OH + conc. H_2SO_4 \xrightarrow{443 \text{ K}} C=C <$$

Dehydration:  $R-OH + conc. H_2SO_4 \xrightarrow{413 \text{ K}} ROR$ 
 $R-OH + Al_2O_3 \xrightarrow{513 \text{ K}} ROR$ 
 $R-OH + Al_2O_3 \xrightarrow{633 \text{ K}} C=C <$ 

Oxidation: Alcohol  $\xrightarrow{[O]}$  Aldehyde/Ketone  $\xrightarrow{[O]}$  Carboxylic acid

*Dehydrogenation* : 1° alcohol Cu/273 K → Aldehyde

Dehydration: 3° alcohol 
$$\xrightarrow{\text{Cu/273 K}}$$
 C=C<

#### **Distinction tests**

- Dichromate test (oxidation) : 1° alcohol → Acid with same number of C-atoms;  $2^{\circ}$  alcohol  $\rightarrow$  Ketone with same number of C-atoms;  $3^{\circ}$  alcohol  $\rightarrow$  No reaction under normal conditions.
- Victor Meyer's test: 1° alcohol → Blood red colour; 2° alcohol → Blue colour; 3° alcohol → Colourless.
- Lucas test(Conc. HCl and ZnCl₂): 1° alcohol → No turbidity; 2° alcohol → Turbidity in 5 minutes; 3° alcohol → Turbidity appears immediately.

#### Some important alcohols

- Rectified spirit is 95% ethanol.
- Absolute alcohol is 100% ethanol.
- Power alcohol is 20:80 mixture of absolute alcohol and gasoline.
- Methylated alcohol or denatured alcohol is ethanol poisoned with methanol and pyridine.

#### **Chemical properties**

• Electrophilic substitution of phenols: Halogenation, sulphonation, nitration, Friedel—Crafts alkylation, etc. occur at o- and p- positions due to activating effect of —OH group.

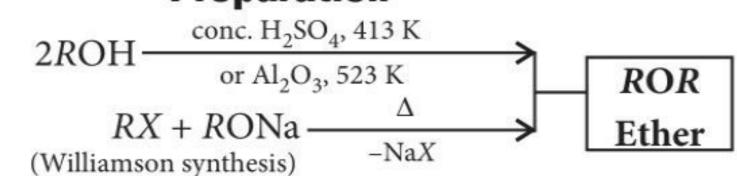
#### Distinguish between alcohols and phenols

Test	Alcohol	Phenol
Litmus test	No effect	Turns blue litmus red
FeCl <sub>3</sub>	No reaction	Blue, violet or green
Coupling reaction	No reaction	Yellow or orange azo dyes
Bromine water test	No reaction	White ppt.

#### **Physical properties**

- Dipolar due to slightly polar C—O bonds.
- B.pts. are lower than isomeric alcohols due to lack of hydrogen bonding.
- Solubility in water ∞ (soluble due to formation of Molecular mass H-bonds with water)
- Fairly soluble in organic solvents.
- Lighter than water.

#### **Preparation**



- Williamson synthesis involves S<sub>N</sub>2 mechanism in case of 1° alkyl halides.
- In the case of 2° and 3° alkyl halides, elimination takes place.
- Dehydration of alcohols for the formation of ethers follows the order:  $1^{\circ} > 2^{\circ} > 3^{\circ}$

#### Uses

Ethers are used as industrial solvents, heat transfer medium (diphenyl ether), flavouring agents and in perfumes.

#### Entropy changes for various types of processes:

Name of the second seco	
Process	$\Delta S$
Isothermal reversible expansion of an ideal gas	$nR \ln \left( \frac{V_2}{V_1} \right)$
Adiabatic reversible expansion	0  as  q = 0
	(isoentropic)
Adiabatic free expansion	<b>≠</b> 0
Isobaric process	$C_p \ln \frac{T_2}{T_1}$
Isochoric process	$C_{\nu} \ln \frac{T_2}{T_1}$

- Second law of thermodynamics: It states that the entropy of the universe is continuously increasing or heat cannot flow on its own from colder to hotter region.
  - For a reversible process,  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$
  - For an irreversible process,  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

#### GIBBS FREE ENERGY

Gibbs free energy: It is the maximum amount of energy available to system to convert into useful work during the process.

- $\triangleright$  G = H TS
- $ightharpoonup \Delta G = \Delta H T\Delta S$  (Gibbs-Helmholtz equation)
- $ightharpoonup \Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$
- $\Delta G^{\circ} = -2.303 \ RT \log K_{eq}$

#### THIRD LAW OF THERMODYNAMICS

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$$\Delta S = S_{TK} - S_{0K} = \int_{0}^{T} \frac{C_{p} dT}{T} = \int_{0}^{T} C_{p} d\ln T$$

From third law of thermodynamics,  $S_{0 \text{ K}} = 0$ , for perfectly crystalline solids.

$$S_{TK} = C_p \ln T = 2.303 C_p \log T$$

For liquids and gases, the absolute entropy at a given temperature T is given by the expression,

$$S = \int_{0}^{T_{f}} \frac{C_{p(s)}dT}{T} + \frac{\Delta H_{f}}{T_{f}} + \int_{T_{f}}^{T_{b}} \frac{C_{p(l)}dT}{T} + \frac{\Delta H_{vap}}{T_{b}} + \int_{T_{h}}^{T} \frac{C_{p(g)}dT}{T} + \frac{\Delta H_{vap}}{T_{b}}$$



#### MCQs Type

- 1. For the reaction  $X_2Y_{4(l)} \longrightarrow 2XY_{2(g)}$  at 300 K the values of  $\Delta U$  and  $\Delta S$  are 2 kcal and 20 cal K<sup>-1</sup> respectively. The value of  $\Delta G$  for the reaction is
  - (a) -3400 cal
- (b) 3400 cal
- (c) -2800 cal
- (d) 2000 cal.
- 2. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor (*Z*) is
  - (a) Z < 1 and repulsive forces are dominant
  - (b) Z > 1 and attractive forces are dominant
  - (c) Z > 1 and repulsive forces are dominant
  - (d) Z < 1 and attractive forces are dominant.

(NEET 2019)

- 3. If  $\Delta H$  and  $\Delta S$  are positive for a reaction, the reaction will be spontaneous only when
  - (a)  $T\Delta S = \Delta H$
- (b)  $T\Delta S > \Delta H$
- (c)  $T\Delta S < \Delta H$
- (d)  $T\Delta S$  is negative.
- 4. Changes in a system from an initial state to the final state were made by a different manner that  $\Delta H$  remains same but q changes because
  - (a)  $\Delta H$  is a path function and q is a state function
  - (b)  $\Delta H$  is a state function and q is a path function
  - (c) both  $\Delta H$  and q are state functions
  - (d) both  $\Delta H$  and q are path functions.
- 5. 22 g solid CO<sub>2</sub> or dry ice is enclosed in a properly closed bottle of one litre. If the temperature of bottle is raised to 25°C to evaporate all the CO<sub>2</sub>, the pressure in bottle is
  - (a) 13.23 atm
- (b) 12.23 atm
- (c) 11.23 atm
- (d) 14.23 atm.

- Which of the following gases has the highest value of rms velocity at 298 K?
  - (a)  $CH_4$
- (b) CO
- (c)  $Cl_2$
- (d)  $CO_2$
- The units of van der Waals' constants a and b respectively are
  - (a)  $L atm^2 mol^{-1} and mol L^{-1}$
  - (b) L atm mol<sup>2</sup> and mol L
  - (c)  $L^2$  atm mol<sup>-2</sup> and mol<sup>-1</sup> L
  - (d)  $L^{-2}$  atm<sup>-1</sup> mol<sup>-1</sup> and L mol<sup>-2</sup>
- 8. For one mole of an ideal gas, which of these statements must be true?
  - (1) *U* and *H* each depends only on temperature.
  - (2) Compressibility factor Z is not equal to 1.
  - (3)  $C_{P, m} C_{V, m} = R$
  - (4)  $dU = C_V dT$  for any process.

  - (a) (2), (3) and (4) (b) (1), (3) and (4)
  - (c) (3) and (4)
- (d) (1) and (3)

(JEE Main 2020)

- The standard boiling point of a liquid is slightly lower than the normal boiling point because
  - (a) 1 bar pressure is slightly less than 1 atm pressure
  - (b) 1 bar pressure is slightly more than 1 atm pressure
  - (c) standard liquids boil faster than normal liquids
  - (d) normal liquids boil faster than standard liquids.
- 10. When 400 mL of 0.2 N solution of a weak acid is neutralised by a dilute aqueous solution of sodium hydroxide under standard conditions, 4.4 kJ amount of heat is liberated. Therefore, the standard enthalpy of neutralisation of this weak acid in kJ equiv<sup>-1</sup> is

- (a) -11 (b) -44 (c) -55 (d) -22
- 11. The types of attractive forces between a polar molecule and a non-polar molecule are
  - (a) dipole-dipole forces
  - (b) hydrogen bonds
  - (c) dipole-induced dipole forces
  - (d) dispersion forces.
- 12. Under isothermal conditions, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is

[Given that 1 L bar = 100 J]

- (a) 30 J
- (b) -30 J
- (c) 5 kJ
- (d) 25 J
- (NEET 2019)

- 13. Which of the following statements is not correct?
  - (a) Viscosity of ethanol is lesser than that of glycol.
  - (b) Viscosity of a liquid decreases with increase in temperature.
  - The variation of viscosity is given by  $\eta = Ae^{(-E/RT)}$
  - (d) Capillary action is due to surface tension of a liquid.
- 14. The statement that is not correct is
  - (a) compressibility factor measures the deviation of real gas from ideal behaviour
  - (b) van der Waals' constant 'a' measures extent of intermolecular attractive forces for real gases
  - (c) critical temperature is the lowest temperature at which liquefaction of a gas first occurs
  - (d) Boyle point depends on the nature of real gas.
- 15. One mole of nitrogen gas at 0.8 atm takes 38 seconds to diffuse through a pinhole, whearas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 seconds to diffuse through the same hole. Calculate the molecular mass of the compound.
  - (a) 252
- (b) 525
- (c) 262
- (d) 380
- 16. van der Waals' equation for one mole of CO<sub>2</sub> gas at low pressure will be

(a) 
$$\left(P + \frac{a}{V^2}\right)V = RT$$
 (b)  $P(V - b) = RT - \frac{a}{V^2}$ 

(b) 
$$P(V-b) = RT - \frac{a}{V^2}$$

$$(c) P = \frac{RT}{V - b}$$

(c) 
$$P = \frac{RT}{V - b}$$
 (d)  $P = \left(\frac{RT}{V - b} - \frac{a}{V^2}\right)$ 

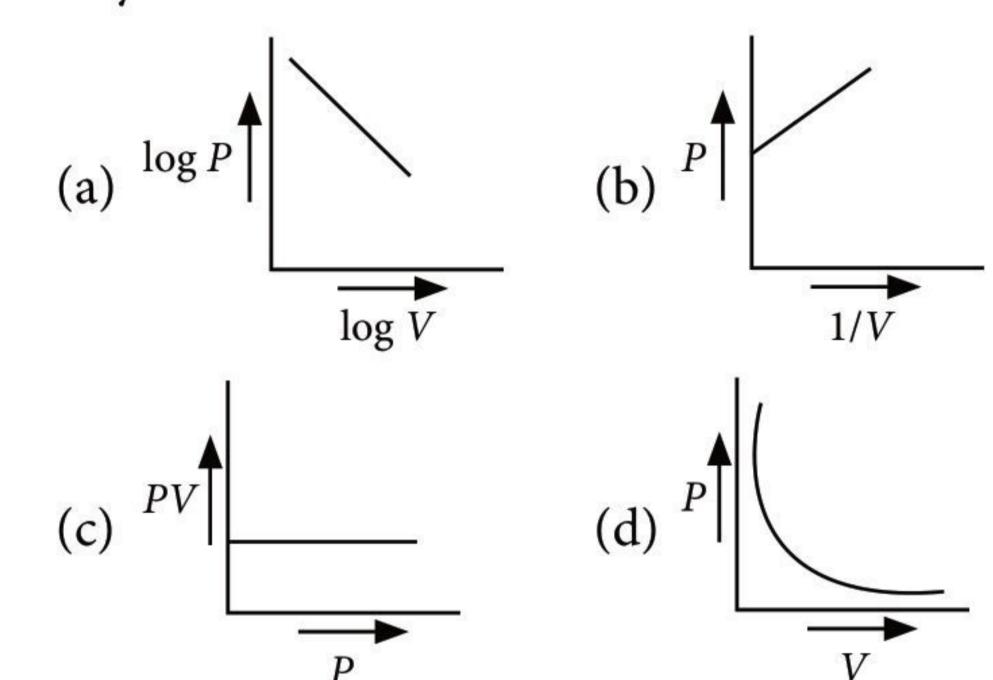
- 17. Which of the following relations holds good when no work is done on the system, but x amount of heat is taken out from the system and given to the surroundings?
  - (a)  $\Delta U = x$
- (b)  $\Delta U = -x$
- (c)  $\Delta U = \Delta E$
- (d)  $\Delta U = -\Delta E$
- 18. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is (specific heat of water liquid and water vapour are 4.2 kJ  $K^{-1}$  kg<sup>-1</sup> and 2.0 kJ  $K^{-1}$  kg<sup>-1</sup>; heat of liquid fusion and vapourisation of water are 334 kJ kg<sup>-1</sup> and 2491 kJ kg<sup>-1</sup>, respectively).

 $(\log 273 = 2.436, \log 373 = 2.572, \log 383 = 2.583)$ 

- (a)  $2.64 \text{ kJ kg}^{-1} \text{ K}^{-1}$  (b)  $9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}$
- (c)  $8.49 \text{ kJ kg}^{-1} \text{ K}^{-1}$  (d)  $7.90 \text{ kJ kg}^{-1} \text{ K}^{-1}$

(JEE Main 2019)

- 19. One gram atom of graphite and one gram atom of diamond were separately burnt to carbon dioxide. The amount of heat liberated were 393.5 kJ and 395.4 kJ respectively. It shows that
  - (a) graphite has greater affinity for oxygen
  - (b) diamond has greater affinity for oxygen
  - (c) graphite is stable than diamond
  - (d) diamond is stable than graphite.
- 20. The incorrect statement among the following is
  - (a) the vapour pressure of a liquid is constant at constant temperature
  - (b) the SI unit of coefficient of viscosity of a liquid is pascal second
  - (c) the surface tension of a liquid decreases with increase of temperature
  - (d) the boiling point of a liquid is the same at all external pressures.
- 21. Which of the following plots does not represent Boyle's law?

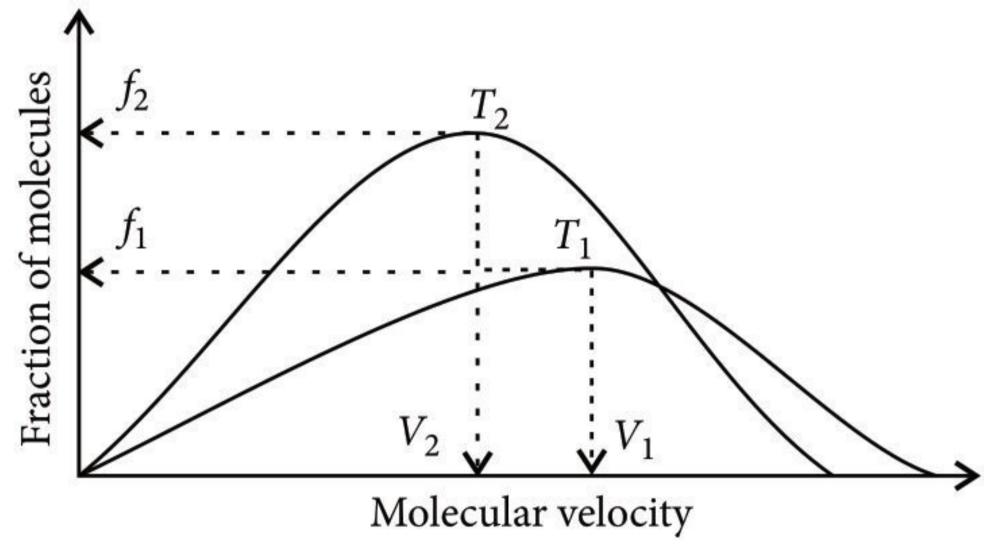


- 22. A solution of 200 mL of 1 M KOH is added to 200 mL of 1 M HCl and the mixture is well shaken. The rise in temperature  $(T_1)$  is noted during this process. The experiment is repeated by using 100 mL of each solution and increase in temperature  $T_2$  is again noted. Which of the following is correct?.
  - (a)  $T_1 = T_2$
  - (b)  $T_2$  is twice as large as  $T_1$ .
  - (c)  $T_1$  is twice as large as  $T_2$ .
  - (d)  $T_1$  is four times as large as  $T_2$ .
- 23. Enthalpy of  $CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH$  is negative.

If enthalpies of combustion of CH<sub>4</sub> and CH<sub>3</sub>OH are x and y respectively, then which of the following relations is correct?

- (a) x > y (b) x < y (c) x = y (d)  $x \ge y$

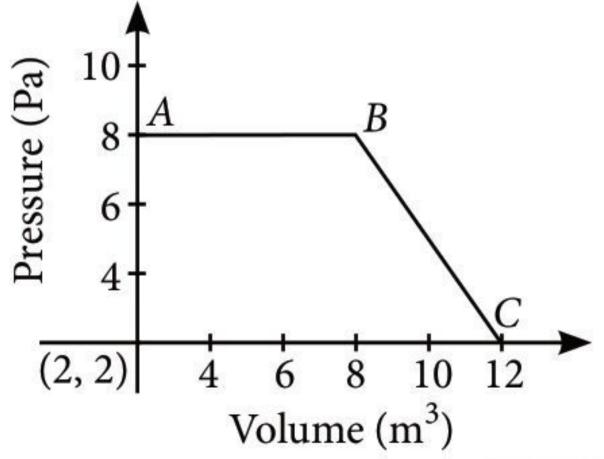
- 24. The heats of neutralization of CH<sub>3</sub>COOH, HCOOH, HCN and  $H_2S$  are -13.2, -13.4, -2.9 and -3.8 kcal per equivalent respectively. The correct increasing order of acid strength is
  - (a)  $HCOOH < CH_3COOH < H_2S < HCN$
  - (b)  $HCN < H_2S < CH_3COOH < HCOOH$
  - (c)  $HCOOH < CH_3COOH < HCN < H_2S$
  - (d)  $CH_3COOH < H_2S < HCN < HCOOH$
- 25. Plot of Maxwell's distribution of velocities is given below:



Which of the following is correct about this plot? (a)  $f_1 > f_2$  (b)  $V_1 < V_2$  (c)  $T_1 < T_2$  (d)  $T_1 > T_2$ 

#### **Numerical Value Type**

- 26. A spherical balloon of radius 3 cm containing helium gas has a pressure of  $48 \times 10^{-3}$  bar. At the same temperature, the pressure, of a spherical balloon of radius 12 cm containing the same amount of gas will be  $\_\_\_ \times 10^{-6}$  bar.
- 27. What volume of oxygen (in litre) at 18°C and 750 torr, can be obtained from 110 g of KClO<sub>3</sub>?
- 28. The standard enthalpies of formation in kJ mol<sup>-1</sup> for  $CO_{2(g)}$ ,  $H_2O_{(l)}$  and  $C_2H_5OH_{(l)}$  are -393.5, -286.0 and -278.0 respectively. The standard enthalpy of combustion of  $C_2H_5OH_{(l)}$  (in kJ mol<sup>-1</sup>) is \_\_\_\_\_.
- 29. The rms velocity of CO gas molecules at 27°C is approximately 1000 m/s. For N<sub>2</sub> molecules at 600 K the *rms* velocity (in m/s) is approximately \_\_\_\_\_.
- 30. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is \_\_\_\_\_ J.



(JEE Main 2020)

#### **SOLUTIONS**

1. (c):  $\Delta H = \Delta U + \Delta n_g RT$   $\Delta H = 2000 + 2 \times 2 \times 300$ [:  $\Delta n_g = 2 - 0 = 2$ , R = 2 cal K<sup>-1</sup> mol<sup>-1</sup>] = 3200 cal

$$\Delta G = \Delta H - T\Delta S = 3200 - (300 \times 20) = -2800 \text{ cal}$$

2. (d):  $V_{\text{ideal}} = V$ ,  $V_{\text{real}} = V - 0.2 \text{ V} = 0.8 \text{ V}$   $Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = 0.8$ 

If value of Z < 1 then attractive forces are dominant.

- 3. **(b)**:  $\Delta G = \Delta H T\Delta S$ For a spontaneous reaction,  $\Delta G =$  negative. If  $\Delta H$  and  $\Delta S =$  +ve, then  $\Delta G$  will be negative when  $T\Delta S > \Delta H$ .
- 4. (b)
- 5. (a): For CO<sub>2</sub>, w = 22 g; V = 1 litre, T = 298 K  $PV = \frac{w}{M}RT \; ; P \times 1 = \frac{22}{44} \times 0.0821 \times 298$   $\therefore P_{\text{CO}_2} = 12.23 \text{ atm}$   $\therefore P_{\text{in bottle}} = P_{\text{CO}_2} + \text{atm pressure}$
- = 12.23 + 1 = 13.23 atm6. (a): Root mean square velocity,  $c = \sqrt{\frac{3RT}{M}}$

From the above equation, lower the molecular mass, higher the *rms* velocity.

7. (c): a and b are expressed in terms of the units of P and V.

Pressure correction = 
$$P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P'V^2}{n^2} = \frac{\text{pressure} \times (\text{volume})^2}{(\text{mole})^2}$$

Unit of  $a = atm \times (L)^2 mol^{-2}$ 

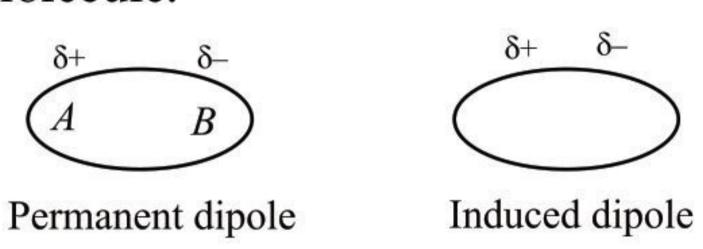
Unit of b is the same as for the molar volume. i.e., L mol<sup>-1</sup>

- 8. **(b)**: Compressibility factor,  $Z = \frac{PV}{nRT}$ For an ideal gas, Z = 1
- 9. (a)
- 10. (c): No. of equivalents of weak acid  $0.4 \times 0.2 = 0.08$ So, amount of heat liberated per equivalent

$$=\frac{4.4}{0.08}=-55 \,\mathrm{kJ \ equiv}^{-1}$$

11. (c): It is the type of force between the polar molecule and a non-polar molecule. Dipole of

polar molecule induces dipole on the electrically neutral molecule.



12. (b): Expansion of a gas against a constant external pressure is an irreversible process. The work done in an irreversible process

= 
$$-P_{\text{ext}} \Delta V = -P_{\text{ext}} (V_2 - V_1) = -2 (0.25 - 0.1)$$
  
=  $-2 \times 0.15 \text{ L bar} = -0.30 \times 100 \text{ J} = -30 \text{ J}$ 

- 13. (c)
- 14. (c): Critical temperature is the temperature above which a gas cannot be liquefied irrespective of the pressure applied.

15. (a): 
$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$
 or  $\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$ 

or 
$$\frac{1}{38} \times \frac{57}{1} = \sqrt{\frac{M_{\text{gas}}}{28}} \times \frac{0.8}{1.6}$$

$$\therefore M_{\text{gas}} = \left[\frac{57}{38} \times \frac{1.6}{0.8}\right]^2 \times 28 \Rightarrow M_{\text{gas}} = 252$$

16. (a): van der Waals' equation for one mole of CO<sub>2</sub> gas is

$$\left[P + \frac{a}{V^2}\right][V - b] = RT$$

At low pressure, V is high hence  $(V - b) \approx V$ .

$$\therefore \left(P + \frac{a}{V^2}\right)V = RT$$

- 17. (b)
- 18. (b):  $H_2O_{(s)} \xrightarrow{\Delta S_1} H_2O_{(l)} \xrightarrow{\Delta S_2} H_2O_{(l)}$ 273 K
  273 K
  373 K  $\xrightarrow{\Delta S_3} H_2O_{(g)} \xrightarrow{\Delta S_4} H_2O_{(g)}$ 373 K
  383 K

$$\Delta S_1 = \frac{\Delta H_{fus}}{273} = \frac{334}{273} = 1.22$$

$$\Delta S_2 = 4.2 \ln \left( \frac{373}{273} \right) = 1.31$$

$$\Delta S_3 = \frac{\Delta H_{vap}}{373} = \frac{2491}{373} = 6.67$$

$$\Delta S_4 = 2.0 \ln \left( \frac{383}{373} \right) = 0.05$$

$$\Delta S_T = 9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

- 19. (c): Less the heat of combustion, more stable is the substance.
- 20. (d): The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. Thus, at different external pressures, the boiling point of the liquid will be different.
- 21. (b)
- 22. (a): Heat produced by 200 meq. of mixture  $= \frac{-13.7 \times 200}{1000} \text{ kcal. This is used to raise the temperature of 400 mL solution say by } T_1.$  Similarly, heat produced by 100 meq. of mixture  $= \frac{-13.7 \times 100}{1000} \text{ kcal. This is used to raise the temperature of 200 mL solution say by } T_2.$  It is evident that  $T_1 = T_2$ .
- 23. (b): (i)  $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ ;  $\Delta H = x$ (ii)  $CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$ ;  $\Delta H = y$ Subtracting eqn. (ii) from eqn. (i) gives the required equation.

$$CH_4 + \frac{1}{2} O_2 \longrightarrow CH_3OH; \Delta H = x - y$$

Since  $\Delta H$  is negative, x < y.

- 24. (b): Stronger the acid, more will be heat of neutralization. Negative sign signifies evolution of heat.
- 25. (d): In Maxwell's distribution of velocities, the curve shifts forward and downward at higher temperature.

$$T_1 > T_2$$
;  $V_1 > V_2$ ;  $f_2 > f_1$ 

**26.** (750) : PV = nRT

No. of moles, 
$$n_1 = \frac{48 \times 10^{-3} \times \frac{4}{3} \pi (3)^3}{RT}$$
 ...(i)

No. of moles, 
$$n_2 = \frac{P \times \frac{4}{3} \pi (12)^3}{RT}$$
 ...(ii)

On comparing eqns. (i) and (ii), we get  $48 \times 10^{-3} \times (3)^3 = P \times (12)^3$  $P = 75 \times 10^{-5} \text{ bar} = 750 \times 10^{-6} \text{ bar}$ 

27. 
$$(32.8)$$
:  $m = 110$  g

$$\left(n = \frac{m}{M}\right) = \frac{110}{122.5} = 0.897 \text{ mol of KClO}_3$$

$$T = 18$$
°C = 291 K,  $P = 750$  torr =  $750/760 = 0.98$  atm  $R = 0.0821$  L atm K<sup>-1</sup> mol<sup>-1</sup>

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

∴ 2 moles of KClO<sub>3</sub> give 3 moles of O<sub>2</sub>

0.897 moles of KClO<sub>3</sub> gives 
$$\frac{0.897}{2} \times 3 = 1.345$$
 moles of O<sub>2</sub>

According to ideal gas equation, PV = nRT

$$V = \frac{nRT}{P} = \frac{1.345 \times 0.0821 \times 291}{0.98} = 32.8 \text{ L}$$

28. 
$$(-1367)$$
:  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ,  
 $\Delta H = -393.5 \text{ kJ mol}^{-1}$  ...(i)

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)},$$
  
 $\Delta H = -286.0 \text{ kJ mol}^{-1} \dots (ii)$ 

$$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow C_2H_5OH_{(l)},$$

$$\Delta H = -278.0 \text{ kJ mol}^{-1} \qquad \dots \text{(iii)}$$

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}, \Delta H = ?$$
...(iv)

(i) × 2 + 3 × (ii) – (iii) will give equations (iv) Hence,  $\Delta H_{\text{comb}} = 2(-393.5) + 3(-286) - (-278)$ = -787 - 858 + 278 = -1367 kJ mol<sup>-1</sup>

**29.** (1414): 
$$c = \sqrt{\frac{3RT}{M}}$$

$$\frac{c_{\text{CO}}}{c_{\text{N}_2}} = \sqrt{\frac{3RT_{\text{CO}}}{M_{\text{CO}}}} \times \frac{M_{\text{N}_2}}{3RT_{\text{N}_2}} \Rightarrow \frac{1000}{c_{\text{N}_2}} = \sqrt{\frac{300}{28}} \times \frac{28}{600}$$
$$\Rightarrow c_{\text{N}_2} = 1000 \times \sqrt{2} = 1000 \times 1.414 = 1414 \text{ m/s}$$

30. (48): Work done by a gas,  $W_{AB} = 6 \times 6 = 36$   $W_{BC} = \frac{1}{2} \times 4 \times 6 = 12$ 

Total work =  $W_{AB} + W_{BC} = 36 + 12 = 48 \text{ J}$ 





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#### TERME OBJECTIVE TYPE QUESTIONS\*

Unit 3

#### Redox Reactions | Hydrogen

#### MCQs

- Which of the following chemical reactions depicts the oxidising behaviour of H<sub>2</sub>SO<sub>4</sub>?
  - (a)  $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$
  - (b)  $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$
  - (c) NaCl +  $H_2SO_4 \rightarrow NaHSO_4 + HCl$
  - (d)  $2PCl_5 + H_5SO_4 \rightarrow 2POCl_3 + 2HCl + SO_5Cl_5$
- 2. Dihydrogen forms three types of hydrides. (i) hydrides are formed by alkali metals and alkaline earth metals. (ii) hydrides are formed by nonmetals and (iii) hydrides are formed by d- and *f*-block elements at elevated temperature. Complex metal hydrides such as (iv) and (v) are powerful reducing agents.
  - (i)
- (ii)
- (iii)
  - $(\mathbf{v})$ (iv)
- (a) Covalent Molecular Saline NaH LiH
- (b) Molecular Covalent Ionic LiAlH<sub>4</sub> CaH<sub>2</sub>
- Covalent Interstitial LiAlH<sub>4</sub> NaBH<sub>4</sub>
- (d) Covalent Saline Interstitial LiAlH<sub>4</sub> NaBH<sub>4</sub>
- 3. Oxidation number of bromine in sequence in  $Br_3O_8$  is

$$O = Br - Br - Br = C$$

$$O = Br - Br = C$$

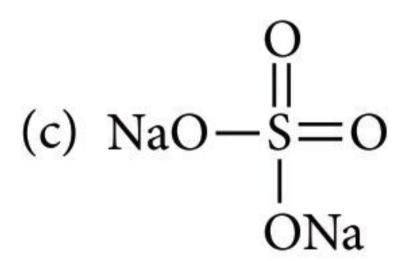
- (a) +8, +6, +8
  - (b) +6, +4, +6
- (c) 0, 0, 0
- (d) + 8, +4, +8
- Study the following reactions and mark the correct properties shown by water.
  - (i)  $SO_3 + H_2O \rightarrow H_2SO_4$
  - (ii)  $Cl_2O_7 + H_2O \rightarrow 2HClO_4$

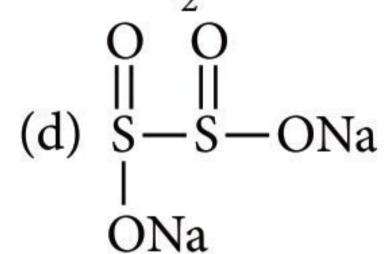
- (iii) CaO + H<sub>2</sub>O  $\rightarrow$  Ca(OH)<sub>2</sub>
- (iv)  $Na_2O + H_2O \rightarrow 2NaOH$
- (a) All oxides react with water to give hydroxides.
- (b) Acidic oxides are formed by metals and basic oxides by non-metals.
- (c) Non-metal oxides combine with water to form acids while metallic oxides combine with water to form alkalies.
- (d) Metal oxides combine with water to form acids while non-metallic oxides combine with water to form alkalies.
- 5.  $MnO_1^{2-}$  (1 mol) in neutral aqueous medium is disproportionated to
  - (a) 2/3 mol of MnO<sub>4</sub> and 1/3 mol of MnO<sub>5</sub>
  - (b)  $1/3 \text{ mol of MnO}_4^-$  and  $2/3 \text{ mol of MnO}_2$
  - (c) 2/3 mol of Mn<sub>2</sub>O<sub>2</sub> and 1/3 mol of MnO<sub>2</sub>
  - (d) 2/3 mol of Mn<sub>2</sub>O<sub>7</sub> and 1/3 mol of MnO<sub>2</sub>.
- 6. What is heavy water?
  - (a)  $H_2O^{18}$  (b)  $D_2O$  (c)  $H_2O^{17}$  (d)  $H_2O$

- 7. The oxidation number of P in  $Mg_2P_2O_7$  is
- (a) +3 (b) +2 (c) +5
- 8. Which of the following is not a redox reaction?
  - (a)  $CaCO_3 \rightarrow CaO + CO_2$
  - (b)  $O_2 + 2H_2 \rightarrow 2H_2O$
  - (c) Na + H<sub>2</sub>O  $\rightarrow$  NaOH +  $\frac{1}{2}$ H<sub>2</sub>
  - (d)  $\operatorname{MnCl}_3 \to \operatorname{MnCl}_2 + \frac{1}{2}\operatorname{Cl}_2$

<sup>\*</sup>Chapterwise practice questions for CBSE Exam Term- I as per the pattern issued by CBSE.

- 9. Which of the following is not an isotope of hydrogen?
  - (a) Protium
  - (b) Ortho- para hydrogen
  - (c) Deuterium
  - (d) Tritium
- 10. Which of the following metals directly combine with hydrogen gas to give a hydride?
  - (a) Au
- (b) Ni
- (c) Ca
- (d) Cu
- 11. The oxidation number of sulphur is −1 in
  - (a) FeS
- (b) FeS<sub>2</sub>





- 12. Which of the following represents calgon?

- (a)  $Na_2Al_2Si_2O_8$  (b)  $Mg_3(PO_4)_2$  (c)  $Na_2[Na_4(PO_3)_6]$  (d)  $Na_2[Mg_2(PO_3)_6]$
- 13. 2.5 moles of hydrazine N<sub>2</sub>H<sub>4</sub> loses 25 moles of electrons to form a new compound X. Assuming that all of the nitrogen appears in the new compound, what is the oxidation state of nitrogen in compound *X*?
  - (a) -1
- (b) -2
  - (c) +3
- (d) +4
- 14. The bond angle and dipole moment of water respectively are
  - (a) 109.5°, 1.84 D
- (b) 107.5°, 1.56 D
- (c) 104.5°, 1.84 D
- (d) 102.5°, 1.56 D
- 15. When KMnO<sub>4</sub> acts as an oxidising agent and ultimately forms  $MnO_4^{2-}$ ,  $MnO_2$ ,  $Mn_2O_3$  and  $Mn^{2+}$ , then the number of electrons transferred in each case respectively is
  - (a) 4, 3, 1, 5
- (b) 1, 5, 3, 7
- (c) 1, 3, 4, 5
- (d) 3, 5, 7, 1
- 16. When electric current is passed through an ionic hydride in molten state
  - (a) hydrogen is liberated at anode
  - (b) hydrogen is liberated at cathode
  - (c) hydride ion migrates towards cathode
  - (d) hydride ion remains in solution.
- 17. The set of numerical coefficients that balances the given equation is

$$K_2CrO_4 + HCl \longrightarrow K_2Cr_2O_7 + KCl + H_2O$$

- (a) 1, 1, 2, 2, 1
- (b) 2, 2, 1, 1, 1
- (c) 2, 1, 1, 2, 1
  - (d) 2, 2, 1, 2, 1

- 18. Hydrogen is
  - (a) electropositive
  - (b) electronegative
  - (c) both electropositive as well as electronegative
  - (d) neither electropositive nor electronegative.
- 19. Among the properties (i) reducing (ii) oxidising (iii) complexing, the set of properties shown by CN<sup>-</sup> ion towards metal species is
  - (a) (i) and (ii)
- (b) (i), (ii) and (iii)
- (c) (i) and (iii)
- (d) (ii) and (iii)
- 20. Which compound is formed when calcium carbide reacts with heavy water?
  - (a)  $C_2D_2$  (b)  $CaD_2$  (c)  $CD_2$

- 21. Which of the following is a decreasing order of oxidation states of the central atoms?
  - (a) PCl<sub>5</sub>, HIO<sub>4</sub>, Cl<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Cl<sub>2</sub>O
  - (b) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Cl<sub>2</sub>O, HIO<sub>4</sub>, PCl<sub>5</sub>
  - (c) HIO<sub>4</sub>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, PCl<sub>5</sub>, Cl<sub>2</sub>O
  - (d) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, HIO<sub>4</sub>, Cl<sub>2</sub>O, PCl<sub>5</sub>
- 22. In which of the following compounds does hydrogen have an oxidation state of -1?

  - (a)  $CH_{4}$  (b)  $NH_{3}$  (c) HCl
- 23. The stoichiometric constants for the reaction  $pCu + qHNO_3 \rightarrow rCu(NO_3)_2 + sNO + tH_2O$ p, q, r, s and t respectively are
  - (a) 3, 3, 3, 2, 3
- (b) 3, 2, 3, 2, 4
- (c) 3, 8, 3, 2, 4
- (d) 2, 3, 3, 3, 2
- 24. At its melting point, ice is lighter than water because
  - (a) on melting ice the H<sub>2</sub>O molecule shrink in size
  - (b) ice crystals have hollow hexagonal arrangement of H<sub>2</sub>O molecules
  - (c) H<sub>2</sub>O molecules are more closely packed in solid state
  - (d) ice forms mostly heavy water on first melting.
- 25. What will be the balanced equation in acidic medium for the given reaction?

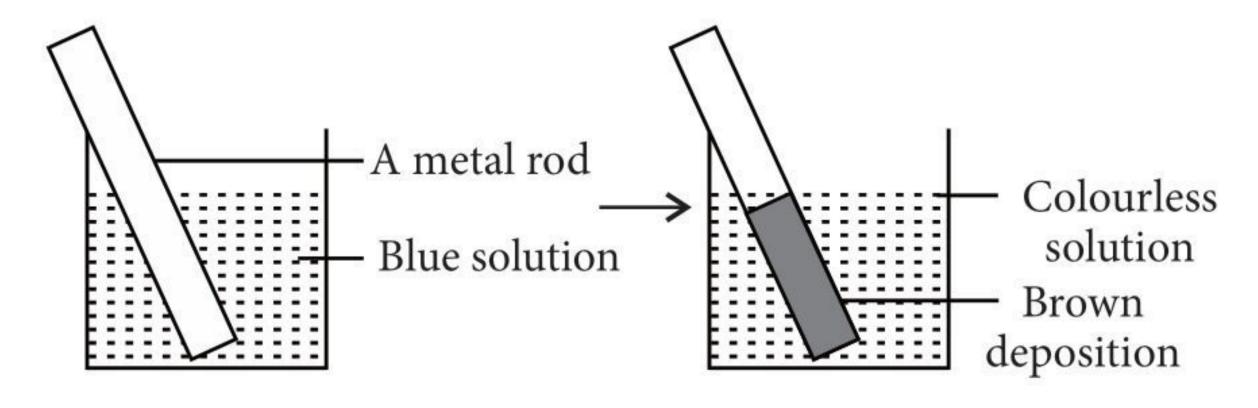
$$\operatorname{Cr}_{2}\operatorname{O}_{7(aq)}^{2-} + \operatorname{SO}_{2(g)} \to \operatorname{Cr}_{(aq)}^{3+} + \operatorname{SO}_{4(aq)}^{2-}$$

- (a)  $\operatorname{Cr}_{2}\operatorname{O}_{7(aq)}^{2-} + 3\operatorname{SO}_{2(g)} + 2\operatorname{H}_{(aq)}^{+} \rightarrow \\ 2\operatorname{Cr}_{(aq)}^{3+} + 3\operatorname{SO}_{4(aq)}^{2-} + \operatorname{H}_{2}\operatorname{O}_{(l)}^{(l)}$
- (b)  $2Cr_2O_{7(aq)}^{2-} + 3SO_{2(g)} + 4H_{(aq)}^+ \rightarrow$ 
  - $4Cr_{(aq)}^{3+} + 3SO_{4(aq)}^{2-} + 2H_2O_{(l)}$

(c) 
$$\operatorname{Cr_2O_{7(aq)}^{2-}} + 3\operatorname{SO}_{2(g)} + 14\operatorname{H}^+ \to (aq) \to 2\operatorname{Cr}^{3+} + 3\operatorname{SO}_{4(aq)}^{2-} + 7\operatorname{H}_2\operatorname{O}_{(l)}$$
 (a)  $\operatorname{Zn_{(s)}} + \operatorname{Cu_{(aq)}^{2+}} \to \operatorname{Zn_{(aq)}^{2+}} + \operatorname{Cu_{(s)}} + 2\operatorname{Ag_{(aq)}^+} + \operatorname{Cu_{(s)}} + 2\operatorname{Ag_{(aq)}^+} + 2\operatorname{Ag_{(s)}^+} + 2\operatorname$ 

$$2Cr_{(aq)}^{3+} + 6SO_{4(aq)}^{2-} + 7H_{2}O_{(l)}$$

- 26. Non-stoichiometric hydrides are formed by
  - (a) palladium and vanadium
  - (b) manganese and lithium
  - (c) nitrogen and fluorine
  - (d) carbon and nickel.
- 27. The number of electrons involved in the conversion of  $MnO_4^-$  to  $MnO_2$  is
  - (a) 3
- (b) 4
- (c) 1
- (d) 2
- 28. The isotopes of hydrogen have almost same chemical properties with a difference in their rates of reactions which is mainly due to
  - (a) their different enthalpy of bond dissociation
  - (b) different electronic configurations
  - (c) different atomic masses
  - (d) different physical properties.
- 29. In the reaction,  $3\text{CuO} + 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3\text{Cu}$ the change of NH<sub>3</sub> to N<sub>2</sub> involves
  - (a) loss of 6 electrons per mol of N<sub>2</sub>
  - (b) loss of 3 electrons per mol of N<sub>2</sub>
  - (c) gain of 6 electrons per mol of N.
  - (d) gain of 3 electrons per mol of  $N_2$ .
- 30. Which one of the following statements about water is false?
  - is oxidized (a) Water during to oxygen photosynthesis.
  - (b) Water can act both as an acid and as a base.
  - (c) There is extensive intramolecular hydrogen bonding in the condensed phase.
  - (d) Ice formed by heavy water sinks in normal water.
- 31. A redox reaction is shown in the diagrams. Identify the reaction.



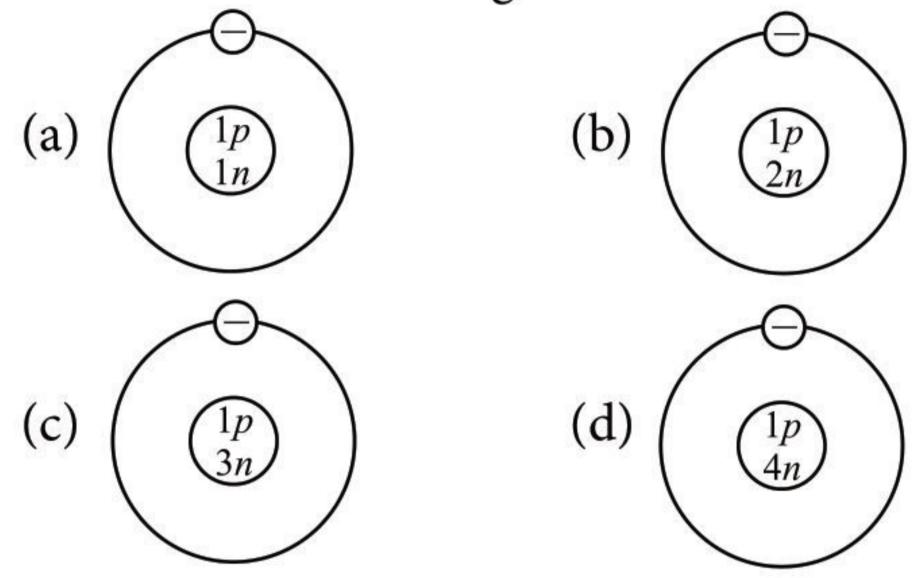
(a) 
$$Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$$

(b) 
$$Cu_{(s)} + 2Ag_{(aq)}^+ \rightarrow Cu_{(aq)}^{2+} + 2Ag_{(s)}$$

(c) 
$$2Ag_{(s)} + Cu_{(aa)}^{2+} \rightarrow 2Ag_{(aa)}^{+} + Cu_{(s)}^{-}$$

(d) 
$$Cu_{(s)} + Zn_{(aa)}^{2+} \rightarrow Cu_{(aa)}^{2+} + Zn_{(s)}^{(s)}$$

- 32. Radioactive elements emit  $\alpha$ ,  $\beta$  and  $\gamma$ -rays and are characterised by their half-lives. The radioactive isotope of hydrogen is
  - (a) protium
- (b) deuterium
- (c) tritium
- (d) hydronium
- 33. In the conversion of  $Br_2$  to  $BrO_3^-$ , the oxidation state of Br changes from
  - (a) +1 to +5
- (b) 0 to -3
- (c) +2 to +5
- (d) 0 to +5
- 34. Which of the following is an atom of tritium?



35. Match the column I with column II with the type of reaction and mark the appropriate choice.

2					
	Column I		Column II		
(A)	$3Mg_{(s)} + N_{2(g)} \xrightarrow{\Delta} Mg_{3}N_{2(s)}$	(i)	Displacement		
(B)	$NaH_{(s)} + H_2O_{(l)} \rightarrow$ $NaOH_{(aq)} + H_{2(g)}$	(ii)	Decomposition		
(C)	$3ClO_{(aq)}^{-} \rightarrow 2Cl_{(aq)}^{-} + ClO^{-}$	(iii)	Combination		
(D)	$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$	(iv)	Disproportionation		

- (a)  $(A) \rightarrow (i), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (iv)$
- (b) (A)  $\rightarrow$  (iv), (B)  $\rightarrow$  (iii), (C)  $\rightarrow$  (ii), (D)  $\rightarrow$  (i)
- (c)  $(A) \rightarrow (ii), (B) \rightarrow (i), (C) \rightarrow (iii), (D) \rightarrow (iv)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (i), (C)  $\rightarrow$  (iv), (D)  $\rightarrow$  (ii)
- 36. Deuterium nucleus contains
  - (a) 1p + 1n
- (b) 2p + 0n
- (c)  $1p + 1e^{-}$
- (d) 2p + 2n

- 37. The pair of compounds in which the metals are in their highest oxidation state is
  - (a) MnO<sub>2</sub>, FeCl<sub>3</sub>
- (b)  $MnO_4^-$ ,  $CrO_2Cl_2$
- (c) MnCl<sub>2</sub>, CrCl<sub>3</sub>
- (d)  $[NiCl_{4}]^{2-}$ ,  $[CoCl_{4}]^{-}$
- 38. Which statement is not correct for ortho and para hydrogen?
  - (a) They have different boiling points.
  - (b) Pure *ortho* hydrogen can be prepared by cooling nearly to absolute zero but pure para hydrogen cannot be prepared.
  - (c) They differ in their nuclear spin.
  - (d) The ratio of ortho to para hydrogen changes with change in temperature.
- 39. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is

- (a) +2 (b) +3 (c) +4 (d) +5
- **40.** The O–H bond length in water molecule is about
  - (a) 95.7 pm
- (b) 100 pm
- (c) 103.2 pm
- (d) 90.5 pm
- 41. A compound contains atoms X, Y and Z. The oxidation number of X is +2, Y is +5 and Z is -2. The possible formula of the compound is
  - (a)  $XYZ_2$
- (b)  $Y_{2}(XZ_{3})_{2}$
- (c)  $X_3(YZ_4)_2$  (d)  $X_3(Y_4Z)_2$
- 42. When zeolite is treated with hard water, the sodium ions are exchanged with
  - (a) H<sup>+</sup> ions
- (b) H<sup>+</sup> and Ca<sup>2+</sup> ions
- (c) OH and Mg<sup>2+</sup> ions (d) Ca<sup>2+</sup> and Mg<sup>2+</sup> ions.
- 43. The reaction,  $Cl_2 \longrightarrow Cl^- + ClO_3^-$  is
  - (a) oxidation
- (b) reduction
- (c) disproportionation (d) all of these.
- 44. Why do calcium ions make water hard but sodium ions do not?
  - (a) Calcium forms insoluble compounds with stearate ions present in soap.
  - (b) Sodium forms insoluble compounds with stearate ions present in soap.
  - (c) Calcium forms soluble compounds with stearate ions present in soap.
  - (d) Both calcium and sodium forms insoluble compounds with stearate ions present in soap.
- 45. 2.5 moles of hydrazine N<sub>2</sub>H<sub>4</sub> loses 25 moles of electrons to form a new compound X. Assuming that all of the nitrogen appears in the new compound, what is the oxidation state of nitrogen in compound *X*?
  - (a) -1
- (b) -2
- (c) +3
- (d) +4

- 46. In solid ice, oxygen atom is surrounded
  - (a) tetrahedrally by 4 hydrogen atoms
  - (b) octahedrally by 2 oxygen and 4 hydrogen atoms
  - (c) tetrahedrally by 2 hydrogen and 2 oxygen atoms
  - (d) octahedrally by 6 hydrogen atoms.
- 47. Match the compounds given in column I with oxidation states of carbon given in column II and mark the appropriate choice.

Column I		Column II	
(A)	$C_6H_{12}O_6$	(i)	+3
(B)	CHCl <sub>3</sub>	(ii)	-3
(C)	CH <sub>3</sub> CH <sub>3</sub>	(iii)	+2
(D)	(COOH) <sub>2</sub>	(iv)	0

- (a)  $(A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (i)$
- (b)  $(A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)$
- (c)  $(A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (iv), (D) \rightarrow (i)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (ii), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (iv)
- 48. The method used to remove temporary hardness of water is
  - (a) synthetic resins method
  - (b) Calgon's method
  - (c) Clark's method
  - (d) ion-exchange method.
- 49. Arrange the oxides of nitrogen in increasing order of oxidation state of N from +1 to +5.
  - (a)  $N_2O < N_2O_3 < NO_2 < N_2O_5 < NO$
  - (b)  $N_2O < NO < N_2O_3 < NO_2 < N_2O_5$
  - (c)  $N_2O_5 < NO_2 < N_2O_3 < NO < N_2O_3$
  - (d)  $NO < N_2O < NO_2 < N_2O_3 < N_2O_5$
- 50. Match the column I with column II and mark the appropriate choice.

Co	lumn I	Column II	
(A)	NaH	(i) Interstitial hydride	
(B)	CH <sub>4</sub>	(ii) Molecular hydride	
(C)	VH <sub>0.56</sub>	(iii) Ionic hydride	
(D)	$B_2H_6$	(iv)	Electron-deficient hydride

- (a)  $(A) \rightarrow (iii), (B) \rightarrow (iv), (C) \rightarrow (ii) (D) \rightarrow (i)$
- (b)  $(A) \rightarrow (ii), (B) \rightarrow (iv), (C) \rightarrow (iii), (D) \rightarrow (i)$
- (c)  $(A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iv), (D) \rightarrow (iii)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (ii), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (iv)

#### CASE BASED

#### Read the passage given below and answer the following questions:

In redox reactions, disproportionation reaction is an important reaction in which a single species is oxidised as well as reduced simultaneously. In these reactions, the reacting species must have an element which can have three variable oxidation states. Decomposition reaction is also an important reaction in which a molecule or compound breaks down to form two or more atoms or molecules. These are simply reverse of combination reaction.

#### The following questions are multiple choice questions. Choose the most appropriate answer:

- 51. The reaction,  $3ClO_{(aq)}^- \rightarrow ClO_{3(aq)}^- + 2Cl_{(aq)}^-$  is an example of
  - (a) oxidation reaction
  - (b) reduction reaction
  - (c) disproportionation reaction
  - (d) decomposition reaction.
- **52.** In the reaction,

$$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

- (a) bromine is oxidised and carbonate is reduced
- (b) bromine is reduced and water is oxidised
- (c) bromine is neither reduced nor oxidised
- (d) bromine is both reduced and oxidised.
- 53. In the photosynthesis of carbohydrate and oxygen from carbon dioxide and water in presence of sunlight and chlorophyll, which of the following statement is not correct?
  - (a) It involves a redox reaction.
  - (b) CO<sub>2</sub> is reduced to carbohydrates.
  - (c) Water is oxidised to oxygen.
  - (d) CO<sub>2</sub> is oxidised to carbohydrates.
- 54. Addition of oxygen to an element or a compound is termed as
  - (a) oxidation
- (b) reduction
- (c) ionisation
- (d) redox reaction.
- 55. The oxidation state of nitrogen in  $NO_3^-$  is
  - (a) -1
- (b) +2
- (c) +3
- (d) +5

#### Read the passage given below and answer the following questions:

Molecular hydrides are formed mainly by elements of comparatively higher electronegativity as of p-block elements. These hydrides have molecular lattices held together by weak van der Waal's forces. In some cases, hydrogen bonds are formed. The general formula for covalent hydrides is  $XH_{8-n}$  where X stands for the symbol of an element and 'n' is number of valence electrons. The electronegativity difference between hydrogen and the atom bonded to it, determines the properties of covalent hydrides. On moving from left to right in a period, hydrides become increasingly acidic in character. For example NH<sub>3</sub> is a weak base, H<sub>2</sub>O is neutral and HF is acidic.

#### The following questions are multiple choice questions. Choose the most appropriate answer:

- 56. Among CaH<sub>2</sub>, NH<sub>3</sub>, NaH and B<sub>2</sub>H<sub>6</sub>, which are covalent hydrides?
  - (a)  $NH_3$  and  $B_2H_6$
- (b) NaH and CaH,
- (c) NaH and NH<sub>3</sub>
- (d) CaH, and B,H
- 57. The hydrides of the first elements in groups 15-17, namely NH<sub>3</sub>, H<sub>2</sub>O and HF respectively show abnormally high values for melting and boiling points. This is due to
  - (a) small size of N, O and F
  - (b) the ability to form extensive intermolecular H-bonding
  - (c) the ability to form extensive intramolecular H-bonding
  - (d) effective van der Waals' interaction.
- 58. Highest boiling point is of
- (b)  $AsH_3$  (c)  $PH_3$
- (d) SbH<sub>3</sub>
- 59. In complex hydrides, hydride ions act as ligand and are coordinated to metal ions. These hydrides are good reducing agents. Which of the following hydrides is not a complex hydride?
  - (a)  $LiAlH_{4}$  (b)  $NaBH_{4}$  (c)  $(AlH_{3})_{n}$  (d)  $LiBH_{4}$
- 60. Carbon hydrides of the type,  $C_n H_{2n+2}$  do not act as Lewis acid or Lewis base. They behave as normal covalent hydrides because
  - (a) carbon hydrides are electron-rich hydrides
  - (b) carbon hydrides are electron-deficient hydrides
  - (c) carbon hydrides are electron-precise hydrides
  - (d) carbon hydrides are non-stoichiometric hydrides.

#### **ASSERTION & REASON**

In the following questions (Q. No. 61 - 70) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct statement for assertion.

- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- **61. Assertion :** The transfer of electrons from zinc to copper takes place through metal wire connecting the two rods.

**Reason :** Electricity from solution in one beaker to other flows by migration of ions through the salt bridge.

**62. Assertion:** Permanent hardness of water is removed by treatment with washing soda.

**Reason :** Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

**63. Assertion :** HNO<sub>3</sub> acts only as oxidising agent while HNO<sub>2</sub> can act both as a reducing agent and an oxidising agent.

**Reason :** In  $HNO_3$ , oxidation state of nitrogen is +5 which is maximum. In  $HNO_2$ , oxidation state of nitrogen is +3 which can change from -3 to +5.

**64. Assertion**: Saline hydrides are non-volatile, non-conducting and crystalline in solid state.

**Reason**: Saline hydrides are compounds of hydrogen with most of the *p*-block elements. oxidants.

**65. Assertion :** KMnO<sub>4</sub>, KClO<sub>4</sub>, and HNO<sub>3</sub> act as oxidants.

**Reason**: In KMnO<sub>4</sub>, KClO<sub>4</sub> and HNO<sub>3</sub> central atom is in its highest oxidation state.

**66. Assertion**: Melting and boiling points of D<sub>2</sub>O are higher than those of ordinary H<sub>2</sub>O.

**Reason**: D<sub>2</sub>O has lesser degree of association than H<sub>2</sub>O and lower molecular mass, hence higher melting and boiling points.

67. Assertion: Cl<sub>2</sub> gas bleaches the articles permanently.

Reason: Cl, is a strong reducing agent.

**68. Assertion :** When sodium hydride in fused state is electrolysed, hydrogen is discharged at anode.

**Reason**: Sodium hydride is an electrovalent compound in which hydrogen is present as cation.

69. **Assertion**: Oxidation state of hydrogen is +1 in H<sub>2</sub>O while -1 in CaH<sub>2</sub>.

**Reason**: CaH<sub>2</sub> is a metal hydride and for hydrides, hydrogen is assigned the oxidation number of -1.

**70. Assertion :** Soft water lathers with soap but not hard water.

**Reason:** Hard water contains calcium and magnesium salts which react with soap to form insoluble salts which form scum and not lather.

#### SOLUTIONS

1. (a): In the reaction,

In this reaction oxidation number of S decreases by two, thus this is a reduction reaction and  $\rm H_2SO_4$  behaves as oxidising agent.

2. (c)

3. (b): 
$$O = Br - Br - O$$
 $O = Br - Br - O$ 
 $O = O$ 

Oxidation states of three bromines are +6, +4, +6.

- 4. (c): Acidic oxides form acids while basic oxides form alkalies with water.
- 5. (a) :  $MnO_4^{2-}$  disproportionates as

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^{-} + MnO_2 + 4OH^{-}$$

or 
$$MnO_4^{2-} + \frac{2}{3}H_2O \rightarrow \frac{2}{3}MnO_4^- + \frac{1}{3}MnO_2 + \frac{4}{3}OH^-$$

Thus, 1 mole of  $MnO_4^{2-}$  disproportionate to 2/3 mole of  $MnO_4^{-}$  and 1/3 mole of  $MnO_2^{-}$ .

6. (b): D<sub>2</sub>O is known as heavy water.

7. (c) : 
$$Mg_2 P_2 O_7$$
 i.e.,  $2 (+2) + 2(x) + 7(-2) = 0$ 

$$\Rightarrow x = +5$$

8. (a) : 
$$Ca C O_3 \rightarrow Ca O + C O_2$$

No change in oxidation number, hence it cannot be a redox reaction.

- 9. (b): Ortho-para hydrogen are spin isomers of hydrogen. Hydrogen has 3 isotopes: Protium ( ${}_{1}^{1}H$ ), Deuterium ( ${}_{1}^{2}D$ ), Tritium ( ${}_{1}^{3}T$ ).
- 10. (c): Hydrogen directly combines with highly reactive metals to give hydrides.

$$Ca + H_2 \rightarrow CaH_2$$

11. (b): In FeS<sub>2</sub> oxidation number of S is -1.

$$+2 + 2x = 0 \implies x = -1$$

- 12. (c): The complex salt of metaphosphoric acid, sodium hexametaphosphate  $(NaPO_3)_6$  is known as calgon. It is represented as  $Na_2[Na_4(PO_3)_6]$ .
- 13. (c): Let the oxidation no. of N in new compound X be x.

be x.  
i.e., 
$$N_2H_4 \longrightarrow 2N + ne^-$$

Suppose no. of electron lost per mole = n

$$\therefore$$
 2(-2) = 2x + n(-1) or  $n = 2x + 4 = 2(x + 2)$ 

No. of electrons lost per mole = 2(x + 2)

No. of electrons lost by 2.5 mole =  $2.5 \times 2 (2 + x)$ 

Now,  $2.5 \times 2(2 + x) = 25$ 

$$5(2 + x) = 25 \text{ or } 2 + x = 5 \text{ or } x = +3$$

- 14. (c) 15. (c) 16. (a)
- 17. (d): Balanced equation is

$$2K_2CrO_4 + 2HCl \rightarrow K_2Cr_2O_7 + 2KCl + H_2O_1$$

- 18. (c)
- 19. (c): CN<sup>-</sup> forms complexes with metal atom and can donate its electrons to vacant orbital of metal atom. Thus, acts both as complexing agent and reducing agent respectively.
- 20. (a) :  $CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$
- 21. (c) :  $Cl_2O \rightarrow 2x + 1(-2) = 0 \Rightarrow x = +1$

$$Cr_2O_7^{2-} \to 2x + 7(-2) = -2 \Longrightarrow x = +6$$

$$HIO_{4} \to +1 + x + 4(-2) = 0 \Rightarrow x = +7$$

$$PCl_5 \rightarrow x + (-5) = 0 \implies x = +5$$

22. (d)

increased by 2

23. (c): 
$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$
decreased by 3

Multiply Cu term with 3 and N term with 2

 $3Cu + 2HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + H_2O$ Balanced H and O

Dalanceu II anu O

 $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ 

- 24. (b): Ice crystals have open cage like structures.
- 25. (a):  $\operatorname{Cr_2O_7^{2-}} + \operatorname{SO_2} \to \operatorname{Cr^{3+}} + \operatorname{SO_4^{2-}}$  (in acidic solution)

Oxidation half equation:

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$
 ...(i)

Reduction half equation:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
 ...(ii)

Multiplying equation (i) by 3 and adding to eqn. (ii) we get

get  

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

26. (a): Palladium and vanadium form non-stoichiometric (or interstitial) hydrides.

27. (a)

28. (a): Enthalpy of bond dissociation of deuterium is higher (443.35 kJ mol<sup>-1</sup>) than hydrogen (435.88 kJ mol<sup>-1</sup>).

29. (a) : 
$$3\text{CuO} + 2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3\text{Cu}$$
  
 $-6e^-$ 

Loss of 6 electrons for 1 mol of N<sub>2</sub>.

- **30.** (c): In the condensed phase, there is extensive intermolecular hydrogen bonding present in water molecules.
- 31. (a): Zinc rod dipped in blue copper sulphate solution is oxidised to  $Zn^{2+}$  and  $Cu^{2+}$  are reduced to Cu and get deposited on zinc rod.
- **32.** (c) : Nucleides with n/p (neutron-proton) ratio > 1.5 are usually radioactive. For example, tritium (n = 2, p = 1).

33. (d): 
$$Br_2 \rightarrow BrO_3^-$$

For  $Br_2$  oxidation number = 0

For BrO<sub>3</sub> oxidation number,  $x + (-6) = -1 \implies x = +5$ 

34. (b): Tritium is  ${}_{1}^{3}H$  having one proton and two neutrons.

It has no. of protons = 1, no. of electrons = 1, no. of neutrons = 2.

- 35. (d)
- 36. (a): Deuterium is an isotope of hydrogen and its nucleus contains one proton and one neutron.

37. (b) : 
$$MnO_4^-$$
,  $CrO_2Cl_2 \rightarrow +7$ , +6

$$MnO_2$$
,  $FeCl_3 \rightarrow +4$ ,  $+3$ 

$$MnCl_2$$
,  $CrCl_3 \rightarrow +2$ , +3

$$[NiCl_{4}]^{2-}[CoCl_{4}]^{-} \rightarrow +2, +3$$

**38.** (b): Pure *para* hydrogen can be prepared by cooling nearly to absolute zero but pure ortho hydrogen cannot be prepared.

39. (b): 
$$6KI + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

In  $Cr_2(SO_4)_3$ , Cr is in +3 oxidation state.

- 40. (a)
- 41. (c): Sum of oxidation numbers of atoms in it is zero.
- **42.** (d): Zeolites can be used to soften water when Na<sup>+</sup> ions in zeolite are replaced by Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in hard water.

43. (c) : 
$$Cl_2 \longrightarrow Cl^{-1} + ClO_3^-$$
Reduction
Oxidation

44. (a): Calcium forms insoluble compounds with stearate ions present in the soap causing hardening of water.

$$Ca_{(aq)}^{2+} + 2C_{17}H_{35}COO_{(aq)}^{-} \rightarrow (C_{17}H_{35}COO)_{2}Ca$$
Calcium stearate
(Insoluble precipitate)

45. (c): Let the oxidation no. of N in new compound Xbe x.

i.e., 
$$N_2H_4 \longrightarrow 2N + ne^-$$

Suppose no. of electron lost per mole = n

$$\therefore$$
 2(-2) = 2x + n(-1) or  $n = 2x + 4 = 2(x + 2)$ 

No. of electrons lost per mole = 2(x + 2)

No. of electrons lost by 2.5 mole =  $2.5 \times 2 (2 + x)$ 

Now,  $2.5 \times 2(2 + x) = 25$ 

$$5(2 + x) = 25 \text{ or } 2 + x = 5 \text{ or } x = +3$$

46. (a): X-ray studies have shown that in ice, four hydrogen atoms tetrahedrally surround each oxygen atom.

47. (a): 
$$C_6H_{12}O_6: 6x + 12 + (-12) = 0 \Rightarrow x = 0$$

$$CHCl_3: x + 1 + (-3) = 0 \implies x = + 2$$
  
 $CH_3CH_3: x + 3 + x + 3 = 0 \implies x = -3$ 

$$(COOH)_{2}^{3}: x + x + (-4 \times 2) + (+2) = 0 \implies x = +3$$

48. (c)

**49.** (b) : Oxides : 
$$N_2O \rightarrow +1$$
,  $NO \rightarrow +2$   
 $N_2O_3 \rightarrow +3$ ,  $NO_2 \rightarrow +4$ ,  $N_2O_5 \rightarrow +5$ 

50. (d)  
51. (c): 
$$3 \stackrel{+1}{\text{ClO}}^- \rightarrow \stackrel{+5}{\text{ClO}}^-_3 + 2 \stackrel{-1}{\text{Cl}}^-$$

In the given reaction chlorine is getting oxidised ( $ClO^- \rightarrow$  $ClO_3^-$ ) as well as reduced ( $ClO^- \rightarrow Cl^-$ ) simultaneously. Therefore it is a disproportionation reaction.

52. (d): 
$$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^-$$

 $+6HCO_3^-$ 

Here, bromine is both oxidised and reduced.

$$Br_2 \longrightarrow BrO_3^-$$
 (Oxidation)

53. (d): CO<sub>2</sub> is reduced to  $\tilde{C}_6H_{12}O_6$  (carbohydrate).

54. (a)

55. (d): 
$$NO_3^-$$
 i.e.,  $1(x) + 3(-2) = -1 \Rightarrow x = +6 - 1 = +5$ 

56. (a): Non-metal hydrides are covalent hydrides.

59. (c): (AlH<sub>3</sub>), is a polymeric hydride like (BeH<sub>2</sub>),  $(MgH_2)_n$ , etc.

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60. (c): Carbon hydrides with general formula  $C_nH_{2n+2}$  are electron-precise hydrides like  $CH_4$ . They have a complete octet hence they do not behave as Lewis acid or Lewis base.

61. (b)

62. (a) : 
$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + 2NaCl$$
  
 $MSO_4 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + Na_2SO_4$   
(where,  $M = Mg$ , Ca)

63. (a): Since in HNO<sub>2</sub> oxidation state of nitrogen can increase or decrease so, it can act as an oxidising as well as a reducing agent.

64. (c): Saline or ionic hydrides are compounds of hydrogen with most of the s-block metals. However, with p-block metals hydrogen forms molecular or covalent hydrides.

65. (a)

66. (c): D<sub>2</sub>O has higher molecular mass and greater degree of association than H<sub>2</sub>O and thus higher melting and boiling points.

67. (c): Cl<sub>2</sub> is an oxidising agent. It bleaches the articles permanently by oxidation in presence of moisture.

68. (c): Sodium hydride is an electrovalent compound in which hydrogen is present as an anion H which is discharged at anode on electrolysis.

$$NaH \rightleftharpoons Na^+ + H^-$$

$$Na^+ + e^- \rightarrow Na$$
 (cathode)

$$2H^- - 2e^- \rightarrow H_2$$
 (anode)

69. (a)

70. (a) : 
$$2RCOONa + Ca^{2+} \rightarrow (RCOO)_2Ca + 2Na^+$$
  
 $2RCOONa + Mg^{2+} \rightarrow (RCOO)_2Mg + 2Na^+$ 

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Unit

#### Surface Chemistry | General Principles and **Processes of Isolation of Elements**

**Surface Chemistry** 

#### ADSORPTION

It is the tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid).

Adsorption	Absorption	
E STATE OF THE STA		
It is the phenomenon of higher concentration of particles of gas or liquid on the surface of the solid.	It is the phenomenon in which the particles of gas or liquid get uniformly distributed throughout the body of the solid.	
The concentration on the surface of the adsorbent is different from that in the bulk. It is a surface phenomenon.		
Rate is initially high but afterwards decreases till the equilibrium is achieved. <i>e.g.</i> , : Water vapours are adsorbed by silica gel.	It occurs at uniform rate.  e.g., : Water vapours are absorbed by anhydrous CaCl <sub>2</sub> .	

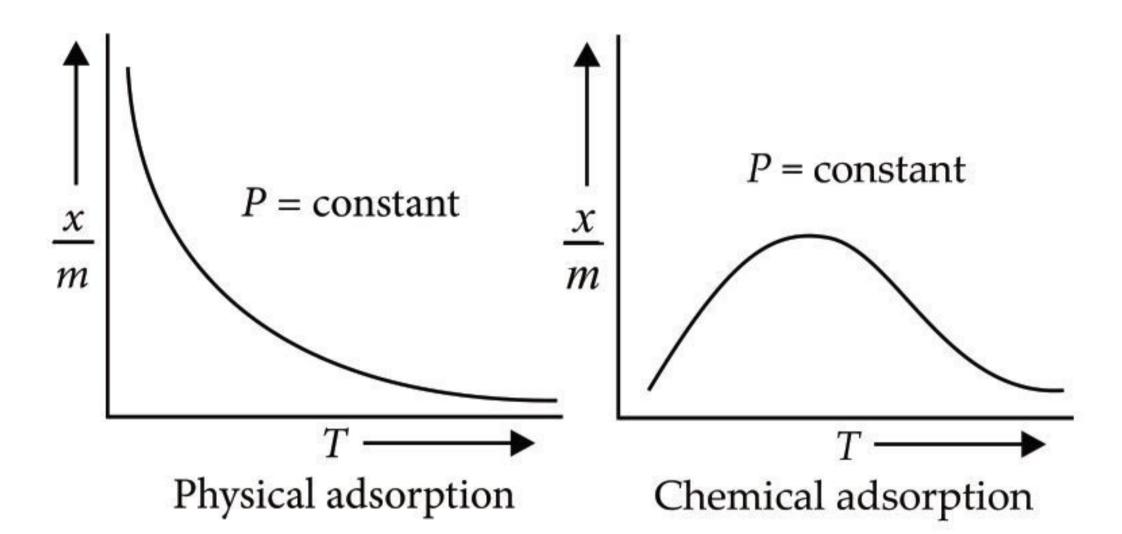
#### **Typical Characteristics of Adsorption Process**

Characteristics	Chemisorption	Physisorption
Material Specificity (Variation between substrates of different chemical composition)		Slight dependence upon substrate composition.
Temperature Range (Over which adsorption occurs)	Virtually unlimited (But a given molecule may effectively adsorb only over a small range)	Near or below the condensation point of the gas. (e.g., $Xe < 100 \text{ K}$ , $CO_2 < 200 \text{ K}$ )

Adsorption Enthalpy	Wide range (related to the chemical bond strength) typically 40 - 800 kJ mol <sup>-1</sup>	Related to factors like molecular mass and polarity.  - typically 5-40 kJ mol <sup>-1</sup>
Nature of Adsorption	Often dissociative, may be irreversible.	Non-dissociative, reversible.
Saturation Uptake	Limited to one monolayer.	Multilayer uptake possible.
Kinetics of Adsorption	Very variable - often an activated process.	Fast - since it is a non-activated process.

#### **Adsorption Isobars**

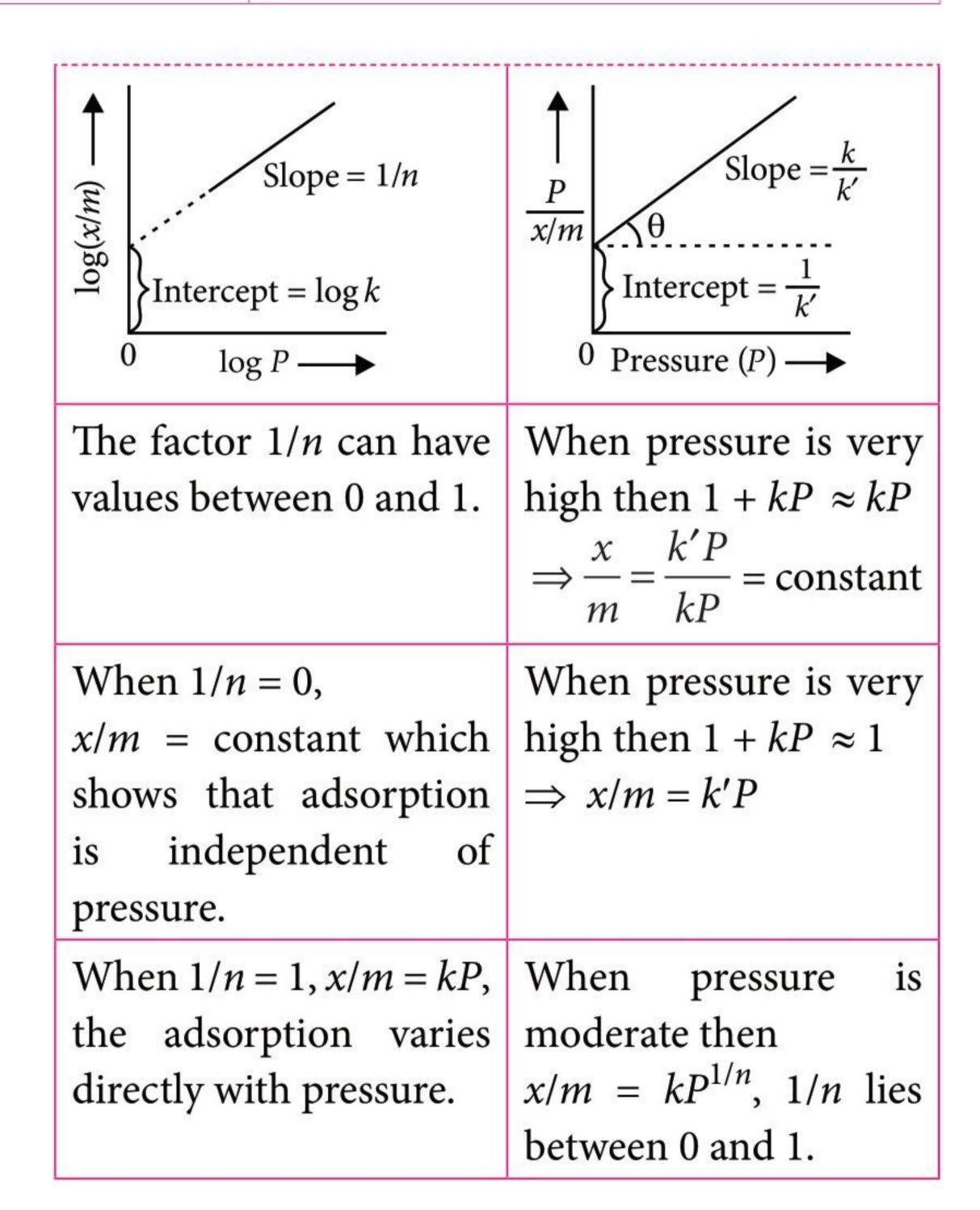
A graph between extent of adsorption (x/m) and temperature (T) at a constant pressure of adsorbate gas is known as *adsorption isobar*.



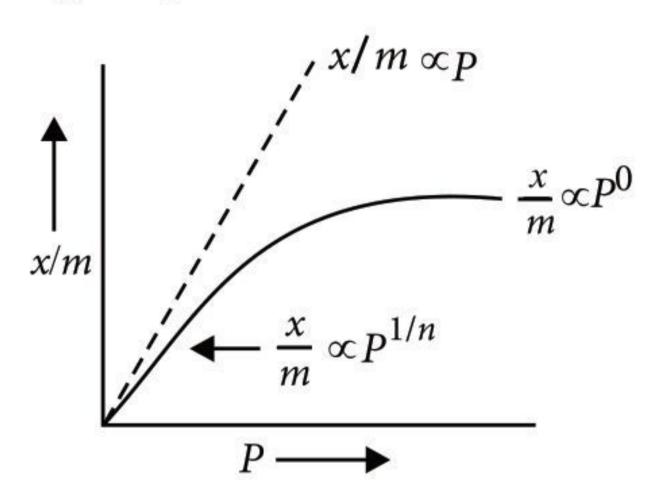
#### **Adsorption Isotherms**

- A graph between the amount of the gas adsorbed per gram of the adsorbent (x/m) and the equilibrium pressure of the adsorbate at constant temperature is called the *adsorption isotherm*.
- ➡ Difference between Freundlich Adsorption Isotherm and Langmuir Adsorption Isotherm :

	Freundlich Adsorption Isotherm	Langmuir Adsorption Isotherm	
	Relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular	theory, Langmuir derived an expression for adsorption	
	temperature. $\frac{x}{m} = k \cdot P^{1/n} (n > 1)$	$\frac{P}{(x/m)} = \frac{1}{k'} + \left(\frac{k}{k'}\right)P$	
20	$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$	$\frac{x}{m} = \frac{k'P}{1+kP}$	



Freundlich equation does not apply to adsorption of gases at higher pressure.



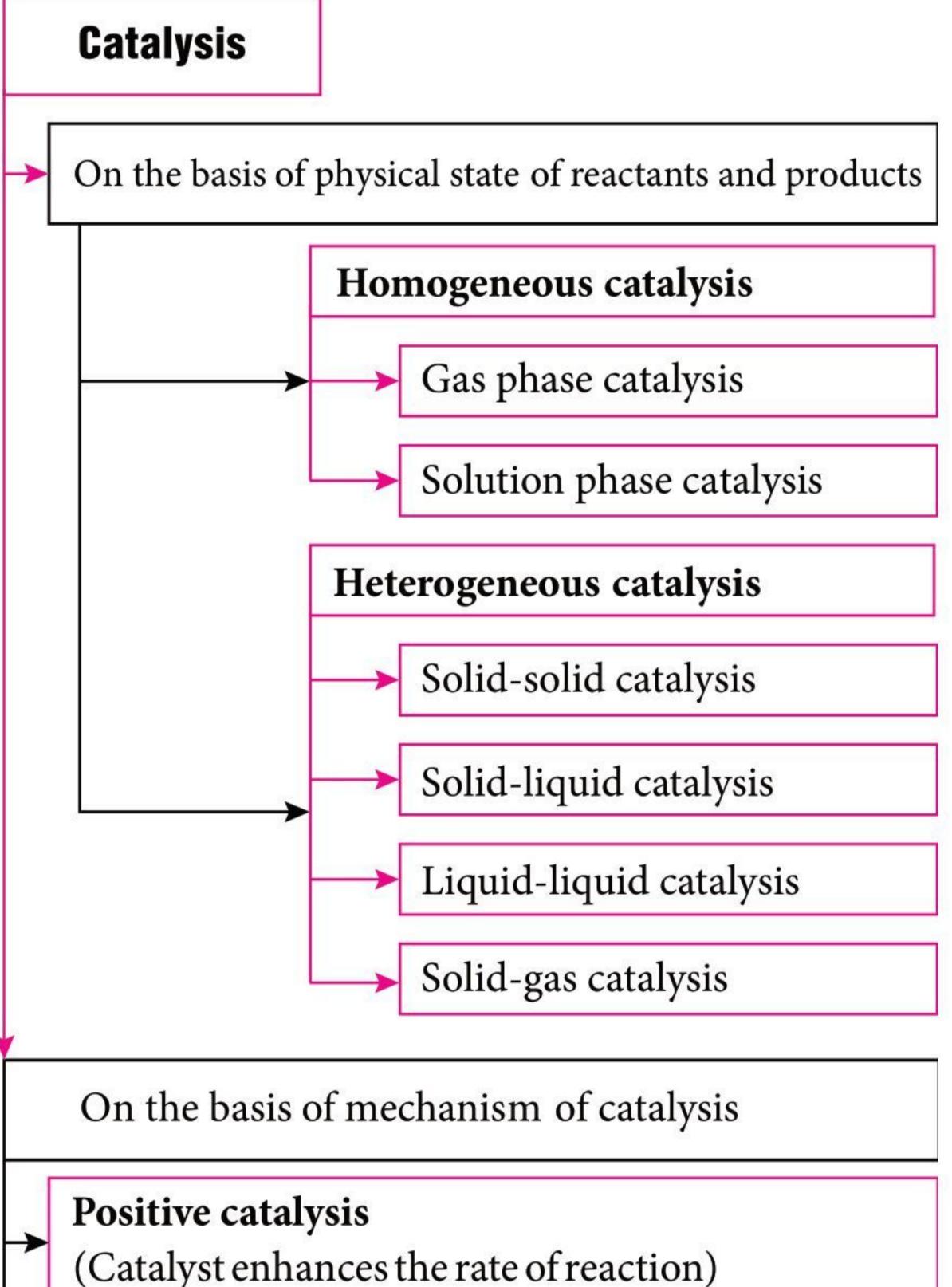
# Quotable Quote 99

"A person who never made a mistake never tried anything new."

Albert Einstein

#### CATALYSIS

The process of enhancing the rate of a chemical reaction by addition of a foreign substance (catalyst) is called catalysis.



Negative catalysis

(Catalyst retards the rate of reaction)

Autocatalysis

(Product of the reaction enhances the rate of reaction)

Induced catalysis

(One reaction increases the rate of other reaction)

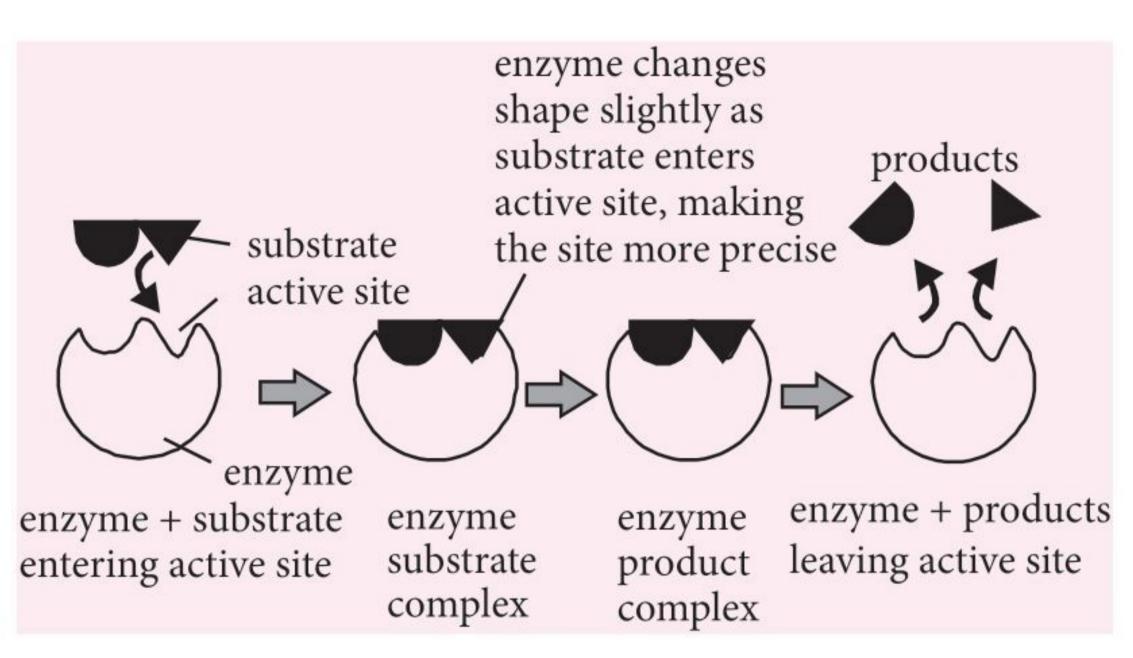
Enzyme catalysis mechanism: Enzyme catalysis reactions are highly specific.

**Step 1**: Binding of enzyme with substrate.

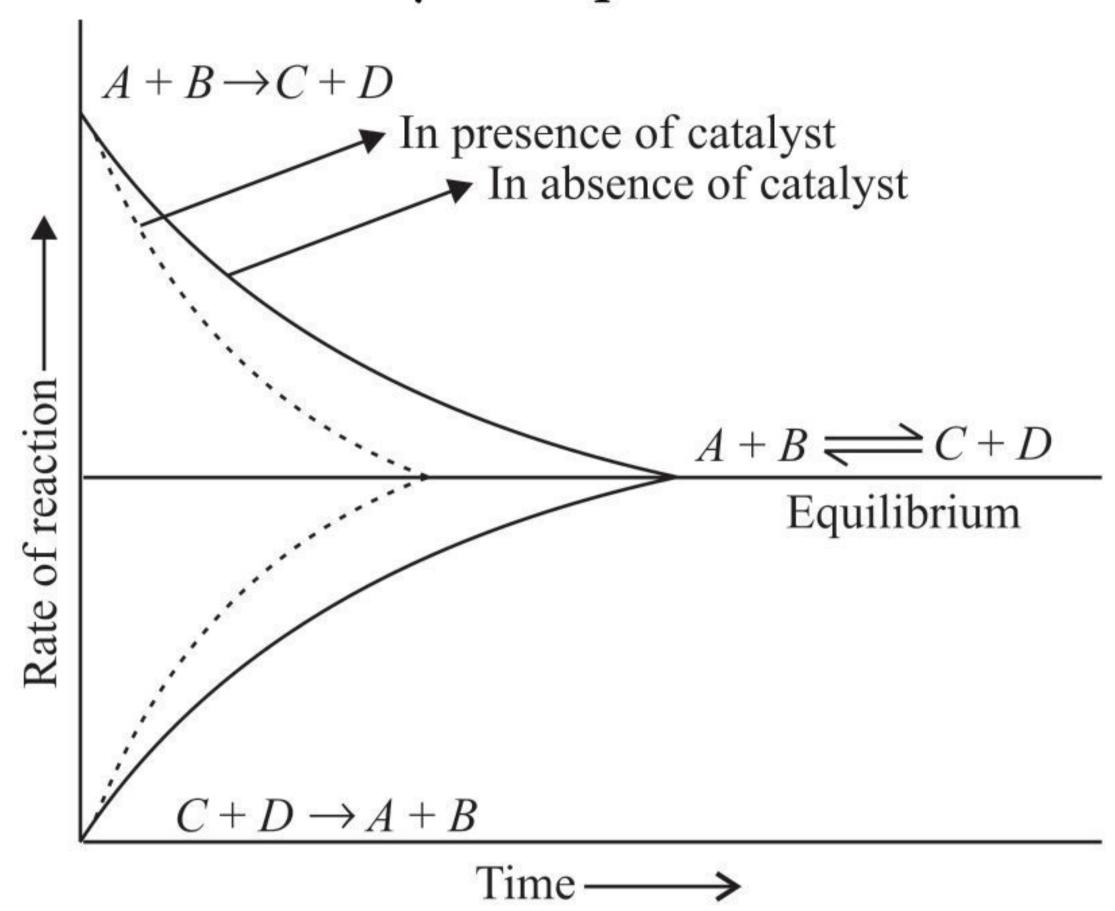
ES (fast) Substrate **Enzyme-Substrate Complex** Enzyme

**Step 2 :** Dissociation of *ES* complex.

ES Enzyme-Substrate **Enzyme-Product** Enzyme Product Complex Association



#### The effect of catalyst on equilibrium:



#### **Notification OJEE 2021**

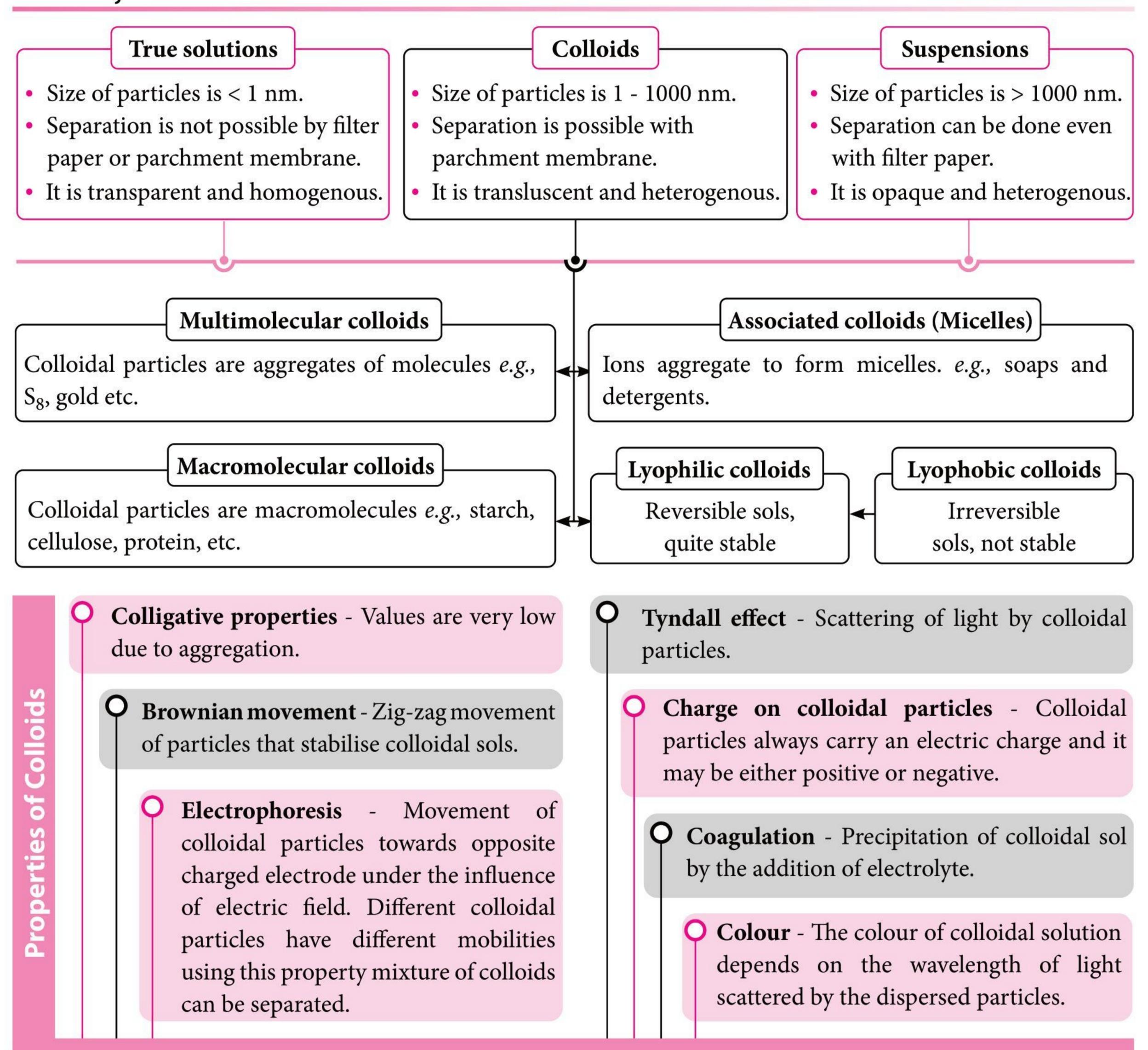
Odisha Joint Entrance Examination (JEE) committee announced the exam schedule for the Odisha Joint Entrance Examination (OJEE 2021). The exams will be held for admission to various undergraduate and postgraduate courses from September 6-18. OJEE was earlier scheduled to be held in June but was postponed due to a coronavirus outbreak.

The entrance examination will be conducted in computer-based test (CBT) mode for all the courses, in three shifts on each day of the examination. The shift-wise complete schedule of the examination is displayed on the official website of OJEE (www.ojee.nic.in).

The entrance exam is being conducted to offer admission to various UG and PG programmes including BPharm, MBA, MCA, M.Tech, M.Arch and Integrated MBA programmes.

The BPharm exam candidates have to prepare for class 12 level Physics, Chemistry, Maths and Biology. On the other hand, the B.Tech (LE-B.Sc) aspirants have to prepare Physics, Chemistry and Maths. The candidates of B.Tech (LE-Diploma) have to prepare Engineering Maths, Engineering Mechanics and Basic Electrical & Electronics Engineering.

#### COLLOIDS, TRUE SOLUTIONS AND SUSPENSIONS



#### Coagulation

- The stability of the colloidal system is due to the existence of charged particles. If the charges are neutralised or destroyed, then the colloidal solution gets precipitated. This is called Coagulation or Flocculation. It can be done by
  - by adding electrolytes
  - by mixing two oppositely charged sols
  - by persistent dialysis
  - by boiling
  - by electrophoresis.

- Coagulation value: The minimum concentration of the electrolyte required in millimoles per litre of solution to cause coagulation or flocculation is called coagulation value.
- Hardy—Schulze rule: According to this rule the coagulating power of the active ion increases with the valency of the active ion.
- Gold number: It is defined as the minimum amount of the protective colloid in milligrams which must be added to 10 mL solution of standard gold sol, which prevents coagulation on adding one mL of 10% NaCl solution.



#### **E**MULSIONS

- Colloidal system in which both the dispersed phase and dispersion medium are liquids is called emulsion.
  - Oil in water type: Oil is dispersed phase and water is dispersion medium *e.g.*, milk, body lotion, etc.
  - Water in oil type: Water is dispersed phase

- and oil is dispersion medium *e.g.*, butter, cold cream, etc.
- Emulsification: Process of making an emulsion.
- Emulsifying agent : Used to stabilize the emulsion *e.g.*, soaps and detergents.
- Demulsification: Separating the two components of an emulsion. Methods used are boiling, freezing, changing pH.

#### **General Principles and Processes of Isolation of Elements**

#### OCCURRENCE OF METALS

- Metals generally occur in earth crust in the form of their compounds. Some of their salts are found in sea water. Most metals are found in combined state.
  - Minerals: The combined state in which the metal occurs in the earth's crust is known as mineral, e.g., bauxite, rock salt, etc.
  - ➤ Ores: Minerals which are rich in metal and from which the metals can be extracted conveniently and profitably. All ores are minerals but all minerals are not ores.
  - The earthy impurities such as sand, clay, rocks, etc., associated with ore are collectively known as *gangue* or *matrix*.

#### **Classification of Ores**

Types of Ore	Ore or Mineral	Composition	Metal Present
Oxide	Bauxite	$Al_2O_3 \cdot 2H_2O$	Al
	Cuprite	Cu <sub>2</sub> O	Cu
	Haematite	$Fe_2O_3$	Fe
	Zincite	ZnO	Zn
	Tinstone or Casseterite	$SnO_2$	Sn
	Pyrolusite	$MnO_2$	Mn
	Pitch blende	$U_3O_8$	U
	Rutile	$TiO_2$	Ti
Sulphide	Copper pyrites	CuFeS <sub>2</sub>	Cu, Fe
	Copper glance	Cu <sub>2</sub> S	Cu
	Zinc blende	ZnS	Zn
	Cinnabar	HgS	Hg

	Galena	PbS	Pb
	Argentite or Silver glance	Ag <sub>2</sub> S	Ag
Carbonate	Magnesite	$MgCO_3$	Mg
	Dolomite	CaCO <sub>3</sub> ·MgCO <sub>3</sub>	Mg
	Calamine	ZnCO <sub>3</sub>	Zn
	Malachite	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	Cu
	Limestone	CaCO <sub>3</sub>	Ca
	Azurite	Cu(OH) <sub>2</sub> ·2CuCO <sub>3</sub>	Cu
	Cerussite	PbCO <sub>3</sub>	Pb
	Siderite	FeCO <sub>3</sub>	Fe
Halide	Rock salt	NaCl	Na
	Carnallite	KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O	Mg

#### METALLURGICAL PROCESSES

- Crushing and grinding of the ore: Involves the breaking of huge lumps into small pieces using crushers or grinders which in turn reduced to fine powder using ball or stamp mill.
- Concentration of ore: Involves the removal of gangue from ore.

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The different methods used in this process are:

**Hydraulic washing:** Based on the difference in the specific gravities of the gangue and the ore particles. Therefore, heavier ore particles settle down while lighter impurities are washed away. For example, oxide ores like haematite, tinstone and native ores of Au, Ag, etc.

**Electromagnetic separation :** Based on the difference in magnetic properties of the gangue and ore particles. Therefore, magnetic particles fall nearer to the roller while non-magnetic particles fall farther off. For example, magnetite (Fe<sub>3</sub>O<sub>4</sub>), haematite (Fe<sub>2</sub>O<sub>3</sub>), wolframite (FeWO<sub>4</sub>), chromite (FeO·Cr<sub>2</sub>O<sub>3</sub>), etc.

**Froth floatation process**: Based on the difference in wetting properties of gangue and ore particles. Therefore, ore particles rise to the surface in the form of froth and impurities remain in water. For example, sulphide ores.

**Leaching :** Based on the difference in chemical properties of gangue and ore particles. Used for extraction of Au, Ag (*Mac Arthur Forest cyanide process*) and pure alumina from bauxite ore (*Baeyer's process*).

- Extraction and isolation of metals: Involves extraction of metal in free state from concentrated ore. The following two chemical processes used are:
  - Calcination: Process of heating the ore strongly below its melting point either in the absence of air or in the limited supply. *e.g.*, carbonate and hydrated oxide ores.

o to

Roasting: Process of heating the ore strongly below the melting point in a sufficient supply of air to bring about its oxidation and remove volatile impurities. *e.g.*, sulphide ores.

Oxidation or de-electronation process

Reduction process

Reduction of calcinated or roasted ore to metal using reducing agent. For example,

- Carbon or carbon monoxide is used for oxides of Fe, Cu, Zn, Mg, Co, etc.
- In aluminothermic reduction or Gold–Schmidt thermite process, a large amount of heat is evolved so that metal is obtained in liquid state.
- Water gas is used for nickel ores.
- Auto-reduction process is used for ores of Pb, Hg, Cu, etc.
- Electrolytic reduction is used for highly electropositive metals.
- Hydrometallurgy or displacement method is used for Ag, Au, etc.

#### THERMODYNAMIC PRINCIPLES OF METALLURGY

- Thermodynamic principles:
  - With the help of thermodynamics, the temperature conditions and suitable reducing agents in the metallurgical processes can be decided.
  - $\triangleright$  Gibb's Helmholtz equation ( $\triangle G^{\circ} = \triangle H^{\circ} T \triangle S^{\circ}$ ), is used to check the feasibility of a reaction.
  - $\geq$   $\Delta G^{\circ}$  < 0 (Spontaneous reaction)
- **Ellingham diagram**: The graphical representation of Gibbs free energy change *vs* absolute temperature for a process is known as *Ellingham diagram*.
- CHEMISTRY TODAY | SEPTEMBER '21

The  $\Delta G^{\circ}$  vs T graphs are straight lines unless the materials melt or vaporise (*i.e.*, change from solid  $\rightarrow$  liquid or from  $liquid \rightarrow gas$ ).

Metal oxide with lower value of  $\Delta G^{\circ}$  is more stable than a metal oxide with higher  $\Delta G^{\circ}$ .

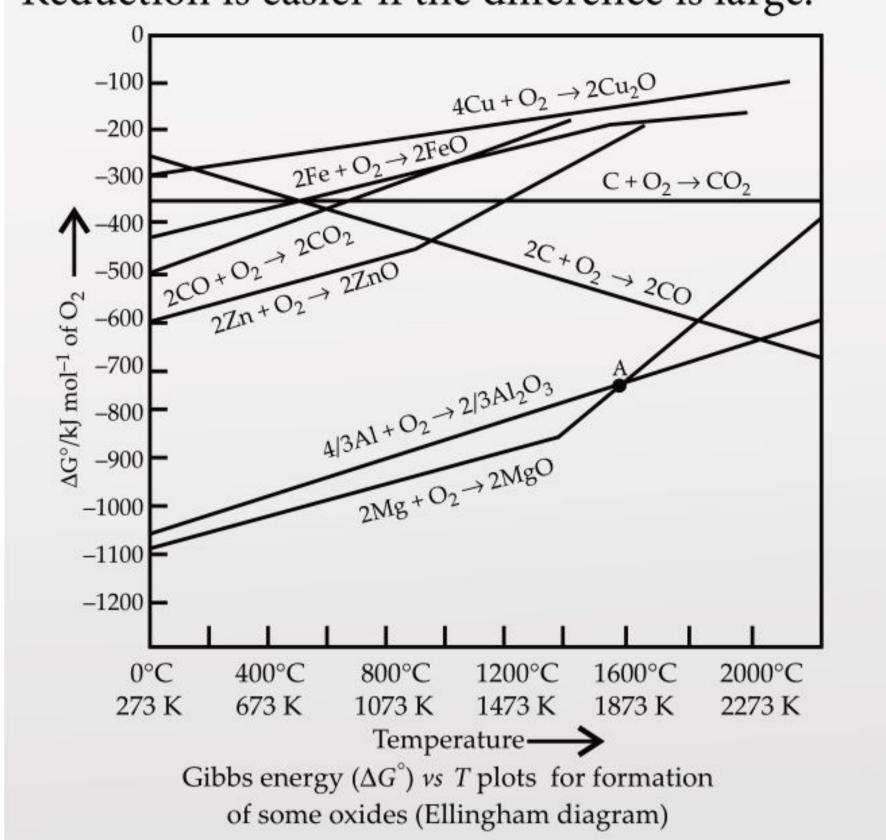
The coupling or combination of oxidation and reduction reactions helps in interpreting whether the given reducing agent can be useful or not.

All the  $\Delta G^{\circ}$  vs T lines have slopes upwards because  $\Delta G^{\circ}$  becomes less and less negative with increase in temperature.

Salient

features

The diagram shows that reduction of the oxide of the elements in upper line is feasible by the elements represented by the lower line. Reduction is easier if the difference is large.



#### REFINING

The different methods used in this process are:

Liquation: Used for low melting metals like Sn, Pb, Hg, Bi, etc.

**Poling:** Used for metals which contain impurities of their own oxides, e.g., Cu.

Electrolytic refining: Used for metals like Cu, Ag, Au, Al which get deposited at cathode and impurities get deposited at anode.

Solution of a soluble metal salt acts as the electrolyte.

Zone refining: Used to produce extremely pure metals (semiconductors) like Si, Ge, Ga, B and In.

Cupellation: Used for metals containing easily oxidisable impurities. e.g., Ag containing Pb impurities.

**Mond's process:** Used for refining of Ni.

$$4\text{CO} + \text{Ni} \xrightarrow{\Delta} \text{Ni}(\text{CO})_4 \downarrow \xrightarrow{180^{\circ}\text{C}} 4\text{CO} + \text{Ni}_{\text{Pure}}$$

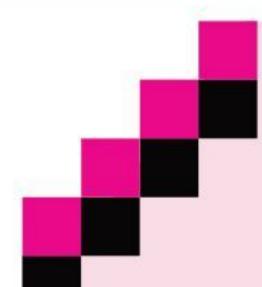
van Arkel method: Used for ultra-pure metals like Ti, Zr which are used in space technology.

$$Ti_{(s)} + 2I_{2(g)} \xrightarrow{523 \text{ K}} TiI_{4(g)} \xrightarrow{1673 \text{ K}} Ti_{(s)} + 2I_{2(g)}$$
Impure

 $Zr_{(s)} + 2I_{2(g)} \xrightarrow{870 \text{ K}} ZrI_{4(g)} \xrightarrow{1800 \text{ K}} Zr_{(s)} + 2I_{2(g)}$ 
Impure

Pure

Pure



# WRAPit up!

#### MCQs Type

Which series of reactions correctly represents chemical relations related to iron and its compound?

(a) 
$$Fe \xrightarrow{O_2, heat} Fe_3O_4 \xrightarrow{CO, 600 \text{ °C}} FeO$$

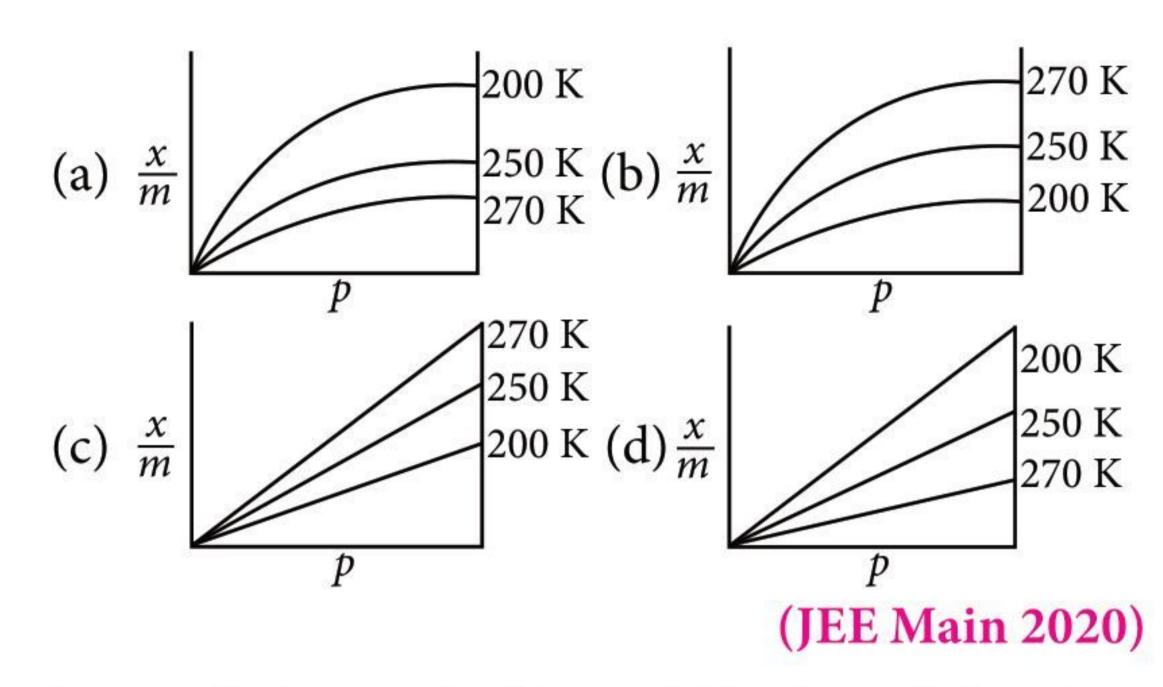
$$\xrightarrow{CO,700 \text{ °C}} Fe$$

(b) 
$$Fe \xrightarrow{\text{dil. H}_2SO_4} FeSO_4 \xrightarrow{\text{H}_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$$

(c)  $Fe \xrightarrow{O_2, heat} FeO \xrightarrow{dil. H_2SO_4} FeSO_4$ 

(d) 
$$Fe \xrightarrow{Cl_2, heat} FeCl_3 \xrightarrow{heat, air} FeCl_2$$

2. Adsorption of a gas follows Freundlich adsorption isotherm. If x is the mass of the gas adsorbed on mass m of the adsorbent, the correct plot of x/mversus p is



- Zone refining method is useful in the refining of
  - Indium
- II. Gallium
- III. Silicon
- IV. Titanium
- (a) Only IV
- (b) Only III
- (c) I, II and III
- (d) I and IV
- 4. Among the electrolytes Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and NH<sub>4</sub>Cl, the most effective coagulating agent for  $Sb_2S_3$  sol is
  - (a)  $Na_2SO_4$
- (b) CaCl<sub>2</sub>
- (c)  $Al_2(SO_4)_3$
- (d) NH<sub>4</sub>Cl
- Which step is not involved in hydrometallurgical process?
  - (a)  $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$
  - (b)  $CuFeS_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2H_2S$
  - (c)  $CuSO_4 + Fe \rightarrow FeSO_4 + Cu$
  - (d)  $CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2$
- Which mixture of the solutions will lead to the formation of negatively charged colloidal [AgI]Isol?
  - (a)  $50 \text{ mL of } 0.1 \text{ M AgNO}_3 + 50 \text{ mL of } 0.1 \text{ M KI}$
  - (b)  $50 \text{ mL of } 1 \text{ M AgNO}_3 + 50 \text{ mL of } 1.5 \text{ M KI}$
  - (c)  $50 \text{ mL of } 1 \text{ M AgNO}_3 + 50 \text{ mL of } 2 \text{ M KI}$
  - (d)  $50 \text{ mL of } 2 \text{ M AgNO}_3 + 50 \text{ mL of } 1.5 \text{ M KI}$

(NEET 2019)

- 7. Which of the following metal is obtained by leaching process using a solution of NaCN and then precipitating the metal by addition of zinc dust?
  - (a) Copper (b) Silver (c) Nickel (d) Iron
- 8. Which of the following statements is correct?
  - (a) True particles are able to pass through filter paper and not in semipermeable membrane.
  - (b) Colloidal particles are able to pass through filter paper and not in semipermeable membrane.
  - (c) Both true and colloidal particles are able to pass through filter paper and semipermeable membrane.
  - (d) Both true and colloidal particles are not able to pass through filter paper and semipermeable membrane.

- The incorrect statement among the following is
  - (a) oxides of highly electropositive metals can be reduced by carbon at high temperature
  - (b) in smelting to get tin from SnO<sub>2</sub>, excess lime must be avoided
  - anodizing is done to produce an oxide coating on a metal surface by making it the anode during electrolysis
  - (d) slag is usually lighter and floats on the surface of the molten metal.
- 10. According to Freundlich adsorption isotherm, which of the following is correct?
  - (a)  $\frac{x}{-} \propto p^1$
- (b)  $\frac{x}{-} \propto p^{1/n}$
- (c)  $\frac{x}{-} \propto p^0$
- (d) All the above are correct for different ranges of pressure.
- 11. The metal used to recover copper from a solution of CuSO<sub>4</sub> is
  - (a) Fe
- (b) Au
- (c) Pt
- (d) Ag
- 12. Rate of physisorption increases with
  - (a) decrease in temperature
  - (b) increase in temperature
  - (c) decrease in pressure
  - (d) decrease in surface area.
- 13. Four metals and their methods of refinement are given
  - (i) Ni, Cu, Zr, Ga
  - (ii) Electrolysis, van Arkel process, Zone refining, Mond's process

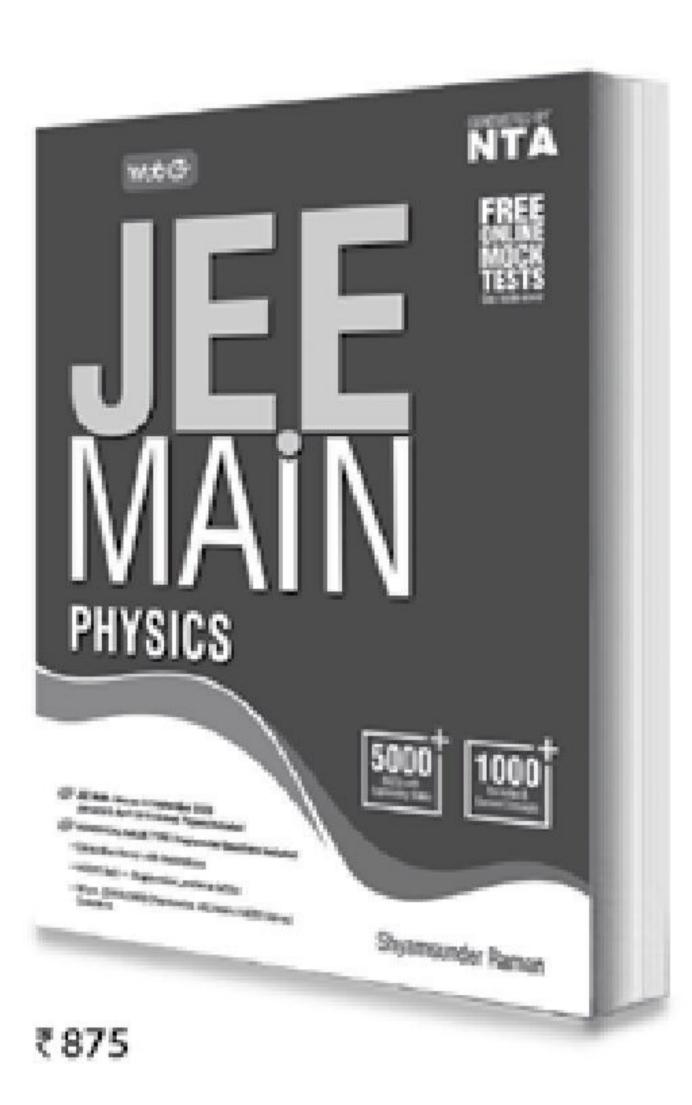
Choose the right method for each

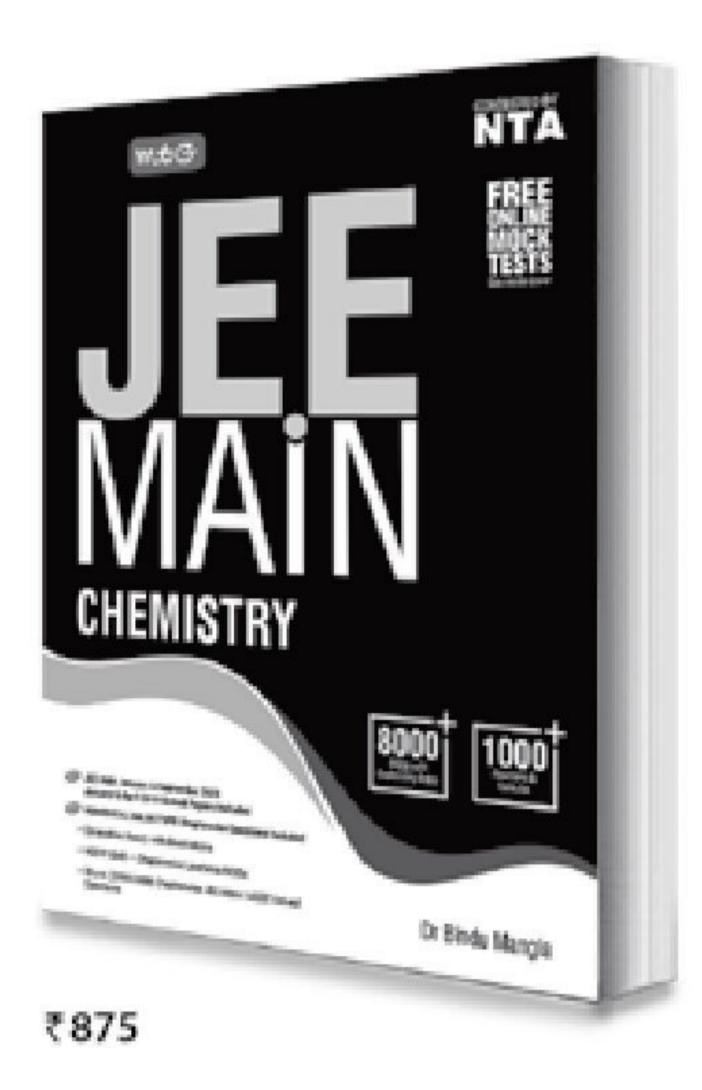
- (a) Ni : Electrolysis, Cu : van Arkel process, Zr: Zone refining, Ga: Mond's process
- (b) Ni : Mond's process, Cu : Electrolysis, Zr: van Arkel process, Ga: Zone refining
- (c) Ni : Mond's process, Cu : van Arkel process, Zr : Zone refining, Ga : Electrolysis
- (d) Ni: Electrolysis, Cu: Zone refining, Zr: van Arkel process, Ga: Mond's process
- 14. Bredig's arc method cannot be used to prepare colloidal solution of which of the following?
  - (a) Pt
- (b) Fe
- (c) Ag
- 15. During extraction of aluminium from bauxite,
  - (a) the concentration of ore is done by gravity separation method
  - (b) molten mixture of aluminium oxide, cryolite and fluorspar is electrolysed

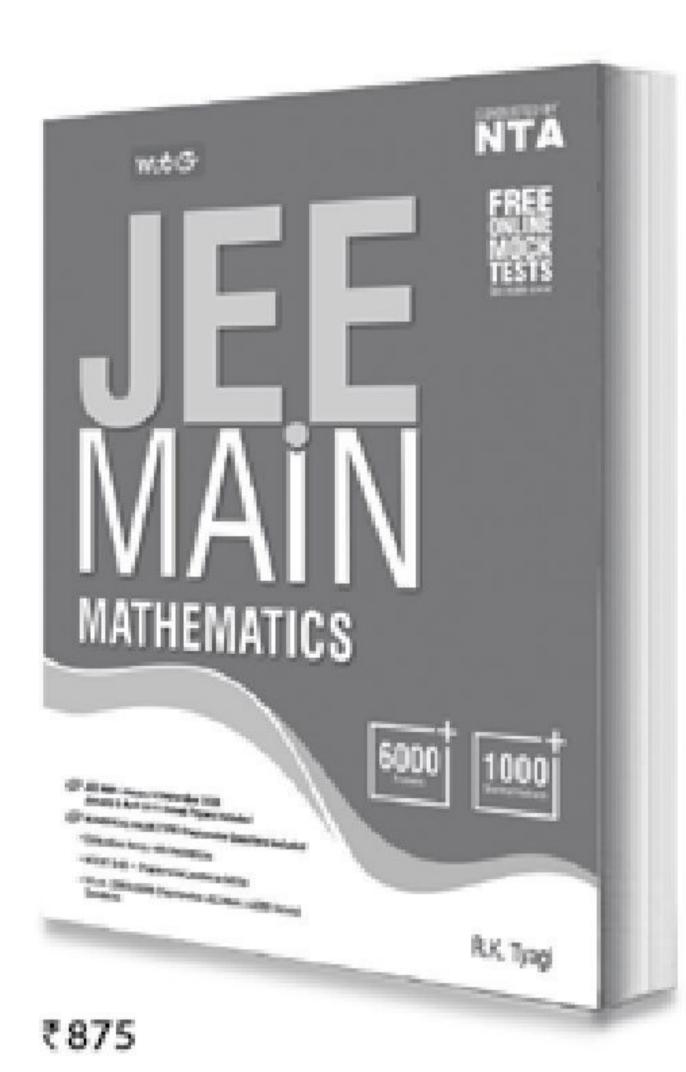
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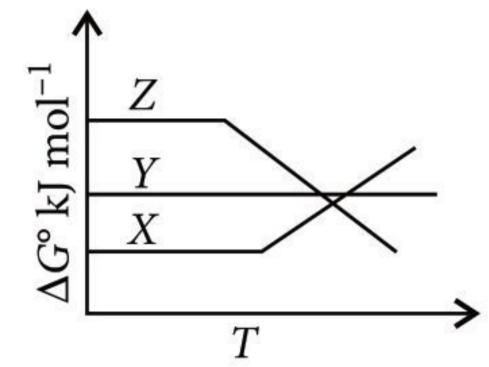
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- (c) impure aluminium is refined by liquation
- (d) molten aluminium is obtained at cathode while fluorine is liberated at anode.
- 16. The process which is responsible for the formation of delta at a place where rivers meet the sea is
  - (a) peptization
- (b) colloidal formation
- (c) emulsification
- (d) coagulation.
- 17. In the following Ellingham diagram X, Y and Zrepresents graph for metal Select oxides. correct option.



- (a) Y will reduce oxide Z.
- (b) *Y* will reduce oxide *X*.
- (c) Z will reduce oxide X.
- (d) Z will reduce oxide Y.
- 18. Which converts alcohols directly into gasoline by dehydration?
  - (a) Zeolite-S
- (b) Zeolite-A
- (c) ZSM-5
- (d) Chabazite.
- 19. Which method of purification is represented by the following equation?

$$\mathrm{Ti}_{(s)} + 2\mathrm{I}_{2(g)} \xrightarrow{523~\mathrm{K}} \mathrm{Ti}\mathrm{I}_{4(g)} \xrightarrow{1700~\mathrm{K}} \mathrm{Ti}_{(s)} + 2\mathrm{I}_{2(g)}$$

- (a) Cupellation
- (b) Poling
- (c) van Arkel
- (d) Zone refining
- 20. Among the colloids, cheese (C), milk (M) and smoke (*S*), the correct combination of the dispersed phase and dispersion medium, respectively is
  - (a) C: solid in liquid, M: liquid in liquid, S: gas in solid
  - (b) *C* : solid in liquid, *M* : solid in liquid, *S* : solid in gas
  - (c) C: liquid in solid, M: liquid in solid, S: solid in gas
  - (d) *C* : liquid in solid, *M* : liquid in liquid, *S* : solid (JEE Main 2019) in gas
- 21. Which one is malachite from the following?
  - (a)  $CuCO_3 \cdot Cu(OH)_2$
- (b) CuFeS<sub>2</sub>
- (c)  $Cu(OH)_2$
- (d)  $Fe_3O_4$
- 22. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is

  - (a) B < D < A < C (b) D < A < C < B
  - (c) C < B < D < A
- (d) A < C < B < D
- 23. Among the reactions (A) (D), the reaction(s) that does/do not occur in the blast furnace during the

- extraction of iron is/are
- (A) CaO + SiO<sub>2</sub>  $\rightarrow$  CaSiO<sub>3</sub>
- (B)  $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$
- (C) FeO + SiO<sub>2</sub>  $\rightarrow$  FeSiO<sub>3</sub>
- (D) FeO  $\rightarrow$  Fe +  $\frac{1}{2}$ O<sub>2</sub>
- (a) (C) and (D)
- (b) (A)
- (c) (A) and (D)
- (d) (D) (JEE Main 2020)
- 24. Which of the following is incorrect?
  - (a) Chemisorption is caused by bond formation.
  - (b) Chemisorption is reversible process.
  - (c) Chemisorption is specific in nature.
  - (d) Chemisorption increases with increase in temperature.
- 25. Identify the following statements as true or false.
  - China clay is an ore of Al.
  - II. Willemite is an ore of sulphide of Cu.
  - III. Malachite is an oxide ore of copper.
  - IV. Siderite is an iron carbonate.
  - (a) TFTT
- (b) TTFT
- (c) TFFT
- (d) TFFF

#### Numerical Value Type

26. For Freundlich adsorption isotherm, a plot of log (x/m) (y-axis) and log p (x-axis) gives a straight line. The intercept and slope for the line is 0.4771 and 2, respectively. The mass of gas, absorbed per gram of adsorbent if the initial pressure is 0.04 atm, is \_\_\_\_\_  $\times 10^{-4}$  g. (log 3 = 0.4771)

(JEE Main 2020)

- 27. The slag obtained during the extraction of copper from copper pyrites is composed mainly of  $\text{Fe}_x \text{Si}_v \text{O}_z$ . What is the value of x + y + z?
- 28. 1 g charcoal adsorbs 100 mL of 0.5 M CH<sub>3</sub>COOH to form a monolayer. As a result molarity of acetic acid reduces to 0.49 M. The surface area covered by each molecule of acetic acid is  $n \times 10^{-19}$  m<sup>2</sup>. The value of n is \_\_\_\_\_\_. Given that surface area of charcoal =  $3.01 \times 10^2$  m<sup>2</sup>/g.
- 29. Among the following, how many metals are common for sulphide ore? Ag, Cu, Sn, Mg, Pb, K, Ca, Au, Pt
- 30. Coagulating value of NaCl and AlCl<sub>3</sub> is 51 and 0.093 respectively. AlCl<sub>3</sub> coagulates x times faster than NaCl. The value of *x* is \_\_\_\_\_.

#### SOLUTIONS

- 1. (a): Formation of  $Fe_3O_4$  through Fe, corresponds to the combustion of Fe and rest part of the reactions correspond to the production of Fe by reduction of  $Fe_3O_4$  in blast furnace.
- 2. (a)
- 3. (c): Zone refining method is used for germanium, silicon, boron, gallium and indium, but titanium is refined by van Arkel method.
- 4. (c)
- 5. (a):  $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$ Bessemerisation
- 6. (b): If colloidal sol of AgI is prepared by adding KI solution to AgNO<sub>3</sub> till KI is in slight excess, iodide ion (I<sup>-</sup>) will be adsorbed on the surface of AgI thereby giving a negative charged sol.

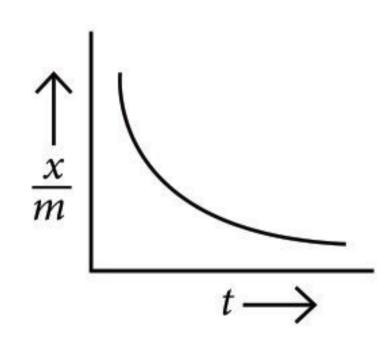
- 7. **(b)**
- 8. (b): Colloidal particles can pass through ordinary filter paper and not through semipermeable membrane.
- 9. (a)
- 10. (d): According to Freundlich adsorption isotherm  $\frac{x}{m} = kp^{1/n}$

1/n can have values between 0 to 1 over different ranges of pressure.

11. (a): Fe is used to remove copper from a solution of CuSO<sub>4</sub>.

$$CuSO_4 + Fe \longrightarrow Cu \downarrow + FeSO_4$$
ppt.

12. (a): With increase of temperature, there occurs a decrease in rate of physisorption. Where, x/m = mass of gas adsorbed per unit mass of adsorbent and t = temperature.



- 13. (b)
- 14. (b) 15. (b) 16. (d)
- 17. (a):  $\Delta G^{\circ}$  of Y is less than Z.
- 18. (c)
- 19. (c): van Arkel method which is also called as vapour-phase refining is used for preparing ultrapure metals like titanium, zirconium, thorium and uranium.

- 20. (d)
- 21. (a): Malachite: CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>.
- 22. (d): The different protecting colloids differ in their protecting powers. Zsigmondy introduced a term called Gold number to describe the protective power of different colloids. Smaller the value of gold number greater will be protecting power of the protective colloid. Thus, protective power of

colloid 
$$\propto \frac{1}{\text{Gold number}}$$

- 23. (a) 24. (b) 25. (c)
- 26. (48): According to Freundlich adsorption isotherm,

$$\left(\frac{x}{m}\right) = K(p)^{1/n}; \log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log p$$

On comparing this with equation of straight line, we get, slope = 1/n = 2

Intercept =  $\log K = 0.4771$ ; K = antilog(0.4771) = 3

$$\therefore \frac{x}{m} = 3(0.04)^2 = 3(4 \times 10^{-2})^2 = 48 \times 10^{-4} \,\mathrm{g}$$

27. (5): The slag obtained during the extraction of copper from copper pyrites is composed mainly of FeSiO<sub>3</sub>.

$$\therefore x = 1; y = 1; z = 3$$
$$x + y + z = 1 + 1 + 3 = 5$$

28. (5): Moles of acetic acid initially present

$$=\frac{0.5\times100}{1000}$$
 = 0.05 moles

Moles of acetic acid after adsorption

$$=\frac{0.49\times100}{1000}$$
=0.049 moles

Acetic acid adsorbed by 1 g of charcoal = 0.050 - 0.049 = 0.001 mole  $= 6.02 \times 10^{20}$  molecules. Surface area of 1 g of charcoal  $= 3.01 \times 10^2$  m<sup>2</sup>

: Surface area of charcoal covered by each molecule

= 
$$(3.01 \times 10^2 \text{ m}^2)/(6.02 \times 10^{20}) = 5 \times 10^{-19} \text{ m}^2$$

29. (3): Ag - Silver glance (Ag<sub>2</sub>S)

Cu - Copper pyrites (CuFeS<sub>2</sub>)

Pb - Galena (PbS)

30. (548):  $\frac{\text{Coagulating power of AlCl}_3}{\text{Coagulating power of NaCl}}$ 

$$= \frac{\text{Coagulating value of NaCl}}{\text{Coagulating value of AlCl}_3} = \frac{51}{0.093} = 548$$

:. AlCl<sub>3</sub> coagulates 548 times faster than NaCl.

# Marm-up!

#### **TERMEI** OBJECTIVE TYPE QUESTIONS\*

Unit 2

#### The p-Block Elements (Group 15 to 18) | Haloalkanes and Haloarenes

#### **MCQs**

- 1. The oxidising property of nitric acid is due to
  - (a) its concentration
  - (b) the positive valency of N
  - (c) its dilution
  - (d) presence of nitrogen in its highest oxidation state.
- 2. Match the column I and column II and mark the appropriate choice.

,	Column I	Column II	
(A)	$CH_3(CH_2)_2CH_2OH$ $\xrightarrow{NaBr}_{H_2SO_4, \Delta}$	(i)	CH <sub>3</sub> CH(Br) (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>
(B)	$(CH_3)_3COH$ Conc. HCl room temp.	(ii)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl
(C)	$CH_3CH(OH)$ $(CH_2)_2CH_3 \xrightarrow{PBr_3}$	(iii)	(CH <sub>3</sub> ) <sub>3</sub> CCl
(D)	$CH_{3}CH_{2}CH_{2}OH \xrightarrow{SOCl_{2}}$	(iv)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> Br

- (a)  $(A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (i), (D) \rightarrow (ii)$
- (b)  $(A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (i)$
- (c)  $(A) \rightarrow (iii), (B) \rightarrow (iv), (C) \rightarrow (i), (D) \rightarrow (ii)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (ii), (D)  $\rightarrow$  (i)
- 3. Which of the following is the correct sequence of the noble gases in their group in the periodic table?
  - (a) Ar, He, Kr, Be, Rn, Xe
  - (b) He, Ar, Ne, Kr, Xe, Rn
  - (c) He, Ne, Kr, Ar, Xe, Rn
  - (d) He, Ne, Ar, Kr, Xe, Rn

 $CH_3OH \xrightarrow{PI_3} X \xrightarrow{KCN} Y \xrightarrow{Hydrolysis} Z$ . The final product in the reaction is

- (a) CH<sub>3</sub>OH
- (b) HCOOH
- (c) CH<sub>3</sub>CHO
- (d) CH<sub>3</sub>COOH
- What causes nitrogen to be chemically inert?
  - (a) High electronegativity of nitrogen
  - (b) Absence of bond polarity
  - (c) Short internuclear distance
  - (d) High bond energy
- 6. The IUPAC name of the compound is
  - (a) 1-fluoro-4-methyl-2-nitrobenzene
  - (b) 4-fluoro-1-methyl-3-nitrobenzene
  - (c) 4-methyl-1-fluoro-2-nitrobenzene
  - (d) 2-fluoro-5-methyl-1-nitrobenzene
- Ionic radii of As<sup>3+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup> follow the order
  - (a)  $As^{3+} > Sb^3 > Bi^{3+}$  (b)  $Sb^{3+} > Bi^{3+} > As^{3+}$
  - (c)  $Bi^{3+} > As^{3+} > Sb^{3+}$  (d)  $Bi^{3+} > Sb^{3+} > As^{3+}$
- An alkyl halide, RX reacts with KCN to give propane nitrile. RX is
  - (a)  $C_3H_7Br$
- (b)  $C_4H_9Br$
- (c)  $C_2H_5Br$
- (d)  $C_5H_{11}Br$
- Identify the incorrect statement with respect to ozone.
  - (a) Ozone is formed in the upper atmosphere by a photochemical reaction than dioxygen.
  - (b) Ozone is more reactive than dioxygen.

\*Chapterwise practice questions for CBSE Exam Term- I as per the pattern issued by CBSE.

- (c) Ozone is diamagnetic whereas dioxygen is paramagnetic.
- (d) Ozone protects the earth's inhabitants by absorbing gamma-radiation.
- 10. The negative part of the addendum (the molecule to be added) adds on to the carbon atom of the double bond containing the least number of hydrogen atoms. This rule is known as
  - (a) Saytzeff's rule (b) Peroxide rule
- - (c) Markovnikov's rule (d) van't Hoff rule
- 11. Identify the correct sequence of increasing number of  $\pi$ -bonds in structures of the following molecules.
  - I.  $H_2S_2O_6$  II.  $H_2SO_3$  III.  $H_2S_2O_5$
- - (a) I, II, III
- (b) II, III, I
- (c) II, I, III
- (d) I, III, II
- 12. Among the isomers of  $C_5H_{11}Cl$ , the chiral species is/are
  - (i) 2,2-Dimethyl-1-chloropropane
  - (ii) 2-Chloropentane
  - (iii) 2-Methyl-2-chlorobutane
  - (iv) 3-Chloropentane
  - (a) (i) and (ii)
- (b) (i), (ii) and (iii)
- (c) (i) and (iii)
- (d) only (ii)
- 13. The coloured discharge tubes for advertisements mainly contain
  - (a) xenon
- (b) helium
- (c) neon
- (d) argon.
- 14. Ethyl alcohol is obtained when ethyl chloride is boiled with
  - (a) alcoholic KOH
- (b) aqueous KOH
- (c) water
- (d) aqueous KMnO₄
- 15. The number of S = O and S OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are
  - (a) (4 and 2) and (4 and 2)
  - (b) (2 and 4) and (2 and 4)
  - (c) (4 and 2) and (2 and 4)
  - (d) (2 and 2) and (2 and 2).
- 16. Methyl bromide reacts with AgF to give methyl fluoride and silver bromide. This reaction is called
  - (a) Fittig reaction
- (b) Swarts reaction
- (c) Wurtz reaction
- (d) Finkelstein reaction.
- 17. Which one of the following statements is not true in respect of properties of interhalogen compounds?
  - (a) They are all covalent compounds.
  - (b) They are volatile solids or liquids except ClF.
  - (c) IF<sub>5</sub> has square pyramidal structure.
  - (d) They are all paramagnetic in nature.

18. In the following pairs of halogen compounds, which compound undergoes faster S<sub>N</sub>1 reaction?

(i) 
$$\stackrel{\text{Cl}}{\swarrow}$$
 and  $\stackrel{\text{Cl}}{\checkmark}$ 

(c) (i) 
$$\langle C_1 \rangle$$
 (ii)  $\langle C_1 \rangle$ 

- 19. Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> react with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Pick out the correct statement from the following.
  - (a) All the halogens react in a similar way.
  - (b) Cl<sub>2</sub> and Br<sub>2</sub> react in a similar way but I<sub>2</sub> reacts differently.
  - (c) Br<sub>2</sub> and I<sub>2</sub> react in a similar way.
  - (d) Cl<sub>2</sub> reacts differently.
- 20. A mixture of two organic compounds was treated with sodium metal in ether solution. Iso-butane was obtained as a product. The two chlorine compounds are
  - (a) methyl chloride and propyl chloride
  - (b) methyl chloride and ethyl chloride
  - (c) iso-propyl chloride and methyl chloride
  - (d) *iso*-propyl chloride and ethyl chloride.
- 21. Nitrogen dioxide is not produced on heating
  - (a)  $KNO_3$
- (b)  $Pb(NO_3)_2$
- (c)  $Cu(NO_3)_2$
- (d) AgNO<sub>3</sub>
- 22. Which of the following is a free radical substitution reaction?

(a) 
$$CH_3$$
  $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_2$   $CH_3$ 

(b) 
$$\bigcirc$$
 + CH<sub>3</sub>Cl  $\xrightarrow{\text{Anhyd. AlCl}_3}$   $\bigcirc$  CH<sub>3</sub>

(c) 
$$CH_2Cl + AgNO_2 \longrightarrow CH_2NO_2$$

- (d)  $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$
- 23. Cane sugar reacts with conc. HNO<sub>3</sub> to give
  - (a)  $CO_2$  and  $H_2O$
- (b) oxalic acid
- (c) CO and H<sub>2</sub>O
- (d) carbonic acid.

- 24. Which of the following halides is not correct according to the name and classification?
  - (a) CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>I 1-Iodo-2, 2-dimethylbutane, Primary haloalkane
  - (b) (CH<sub>3</sub>)<sub>2</sub>CHCH(Cl)CH<sub>3</sub> 2-Chloro-3-methylbutane, Secondary haloalkane
  - (c) CH<sub>3</sub>C(Cl)(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>CH<sub>3</sub> 2-Chloro-2ethylbutane, Secondary haloalkane

CH<sub>3</sub> Cl | | (d) CH<sub>3</sub>—CH<sub>2</sub>—CH—CH—CH<sub>2</sub>—CH<sub>3</sub> – 3-Chloro-4-methylhexane, Secondary haloalkane

- 25. The reaction of KMnO<sub>4</sub> and HCl result in
  - (a) oxidation of Mn in KMnO<sub>4</sub> and production of Cl<sub>2</sub>
  - (b) reduction of Mn in KMnO<sub>4</sub> and production of H<sub>2</sub>
  - (c) oxidation of Mn in KMnO<sub>4</sub> and production of H<sub>2</sub>
  - (d) reduction of Mn in KMnO<sub>4</sub> and production of Cl<sub>2</sub>
- 26. Which of the following statements is true?
  - (a) Allyl chloride is more reactive than vinyl chloride.
  - (b) Vinyl chloride is as reactive as allyl chloride.
  - (c) Vinyl chloride is more reactive than allyl chloride.
  - (d) Both allyl chloride and vinyl chloride are less reactive than chlorobenzene.
- 27. Sea divers go deep in the sea water with a mixture of which of the following gases?
  - (a)  $O_2$  and He
- (b)  $O_2$  and Ar
- (c)  $O_2$  and  $CO_2$
- (d) CO<sub>2</sub> and Ar

28. 
$$\langle \rangle$$
 C1  $\xrightarrow{[X]}$   $\langle \rangle$ 

The reagent [X] may be

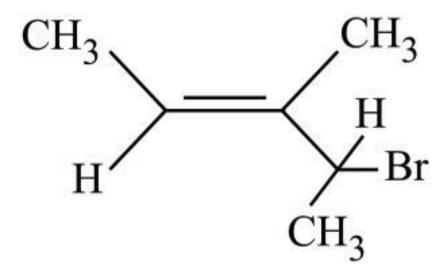
- (a) aq. NaOH
- (b) alc. KOH
- (c)  $(C_2H_5)_3N$
- (d) both (b) and (c).
- 29. The correct order of acidic strength is
  - (a)  $K_2O > CaO > MgO$  (b)  $CO_2 > N_2O_5 > SO_3$
  - (c)  $Na_2O > MgO > Al_2O_3(d)$   $Cl_2O_7 > SO_2 > P_4O_{10}$
- 30. Treatment of ammonia with excess of ethyl chloride will yield
  - (a) diethyl amine
- (b) ethane
- (c) tetraethylammonium chloride
- (d) methyl amine.
- 31. Which one statement about sulphur dioxide gas is incorrect?
  - (a) It has an angular shape.
  - (b) It decolourises acidified potassium permanganate solution.

- (c) Two S O bonds are equal.
- (d) It is a dehydrating agent.
- **32.** The compound that forms racemic products on reaction with aqueous KOH is
  - (a) 3, 4-dimethyl-1-iodopentane
  - (b) 2, 3-dimethyl-3-iodopentane
  - (c) 1-iodo-3-methylpentane
  - (d) 1-iodo-4-methylpentane.
- 33. The structure of XeO<sub>3</sub> is
  - (a) linear
- (b) planar
- (c) pyramidal
- (d) T shaped.

34. Br 
$$\longrightarrow$$
 Cl  $\xrightarrow{\text{Mg/ether}} A \xrightarrow{\text{Na/ether}} B$ , B is

(a)  $\bigcirc$  D

- (b) D—\\\ \\_D
- (c) \
- (d) none of these.
- 35. Which of the following statement is wrong?
  - (a) The stability of hydrides increases from NH<sub>3</sub> to BiH<sub>3</sub> in group 15 of the periodic table.
  - (b) Nitrogen cannot form  $d\pi$ - $p\pi$  bond.
  - (c) Single N—N bond is weaker than the single P—P bond.
  - (d) N<sub>2</sub>O<sub>4</sub> has two resonance structures.
- 36. Which statement is correct?
  - (a) C<sub>2</sub>H<sub>5</sub>Br reacts with alcoholic KOH to form C<sub>2</sub>H<sub>5</sub>OH.
  - (b) C<sub>2</sub>H<sub>5</sub>Br when treated with metallic sodium gives ethane.
  - (c) C<sub>2</sub>H<sub>5</sub>Br when treated with sodium ethoxide forms diethyl ether.
  - (d) C<sub>2</sub>H<sub>5</sub>Br with AgCN forms ethyl cyanide.
- **37.** Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?
  - (a) HF
- (b) HCl
- (c) HBr
- (d) HI
- 38. The IUPAC name of the given compound is

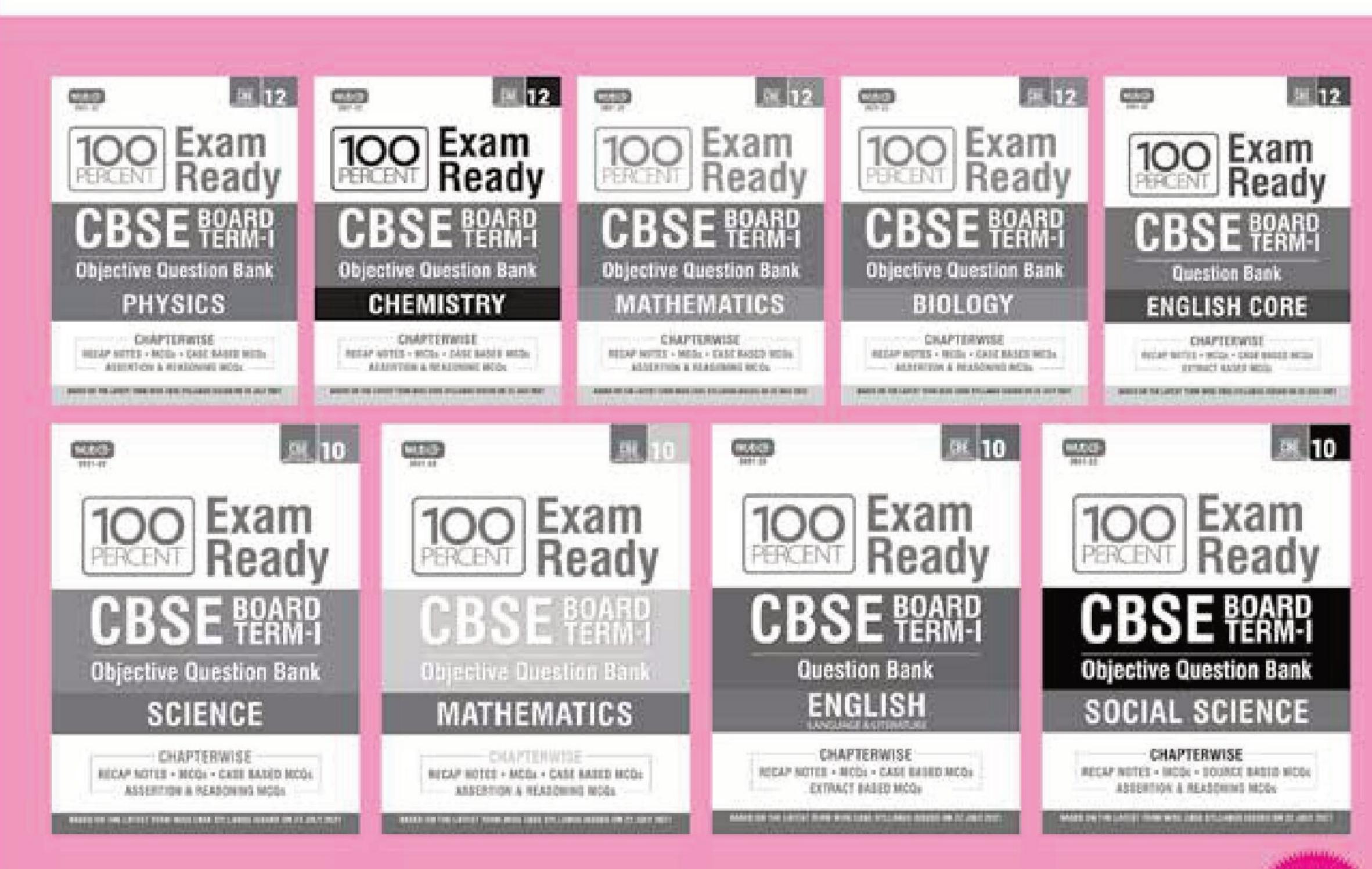


- (a) 3-bromo-2-methylbut-1-ene
- (b) 4-bromo-3-methylpent-2-ene
- (c) 1-bromo-2-methylbut-2-ene
- (d) none of these.



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Available at all leading book shops throughout India. To buy online visit www.mtg.in. For more information or for help in placing your order, call 0124-6601200 or email info@mtg.in 39. Match the column I with column II and mark the appropriate choice.

Column I		Column II		
(A)	$\operatorname{ICl}_4^-$	(i)	Linear	
(B)	$IBr_2^-$	(ii)	Pyramidal	
(C)	$BrO_3^-$	(iii)	T-shaped	
(D)	BrF <sub>3</sub>	(iv)	Square planar	

- (a)  $(A) \rightarrow (iii)$ ;  $(B) \rightarrow (i)$ ;  $(C) \rightarrow (iv)$ ;  $(D) \rightarrow (ii)$
- (b)  $(A) \rightarrow (i)$ ;  $(B) \rightarrow (ii)$ ;  $(C) \rightarrow (iii)$ ;  $(D) \rightarrow (iv)$
- (c)  $(A) \rightarrow (ii); (B) \rightarrow (iv); (C) \rightarrow (iii); (D) \rightarrow (i)$
- (d) (A)  $\rightarrow$  (iv); (B)  $\rightarrow$  (i); (C)  $\rightarrow$  (ii); (D)  $\rightarrow$  (iii)

The products *P* and *Q* are

- (a) *p*-bromonitrobenzene *p*-bromoaniline
- (b) *o*-bromonitrobenzene *o*-bromoaniline
- (c) *o,p*-dibromonitrobenzene *o,p*-dibromoaniline
- (d) *m*-bromonitrobenzene *m*-bromoaniline
- 41. The oxidation state of sulphur in the anions  $SO_3^{2-}$ ,  $S_2O_4^{2-}$  and  $S_2O_6^{2-}$  follows the order

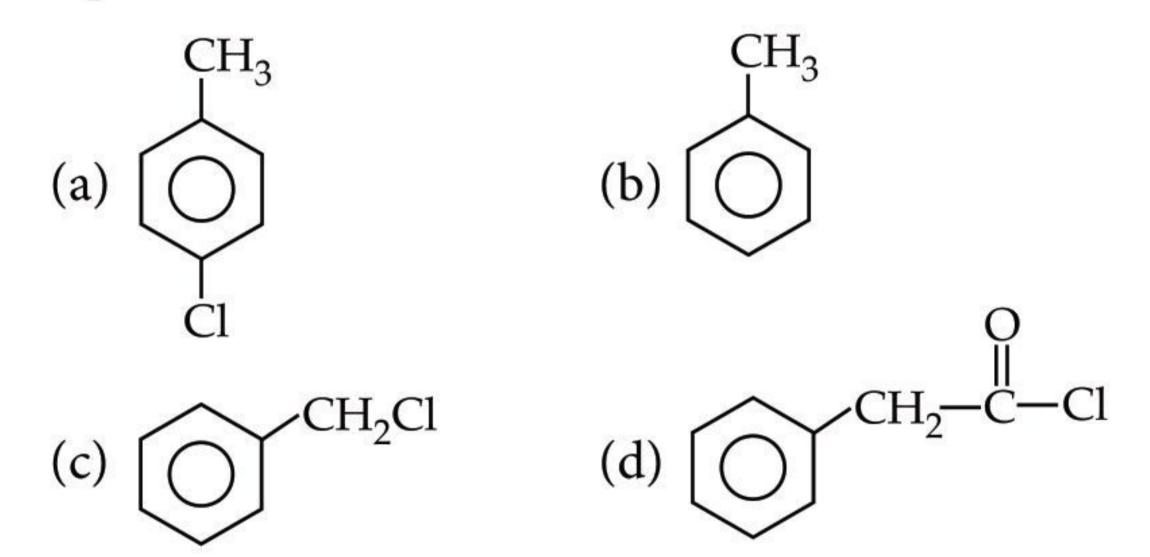
(a) 
$$S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$$

(b) 
$$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$$

(c) 
$$SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$$

(d) 
$$S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$$

42. Which one of the following will react fastest with aqueous NaOH?



**43.** Bond dissociation enthalpy of E — H (E = element) bonds is given below. Which of the compounds will act as strongest reducing agent?

Compound

 $\Delta_{\text{diss}} (E-H)/kJ \text{ mol}^{-1} 389 322 297 255$ 

(a)  $NH_3$  (b)  $PH_3$  (c)  $AsH_3$  (d)  $SbH_3$ 

44.  $CH_3Br + Nu^- \longrightarrow CH_3Nu + Br^-$ 

The decreasing order of the rate of the above reaction with nucleophiles ( $Nu^-$ ) A to D is

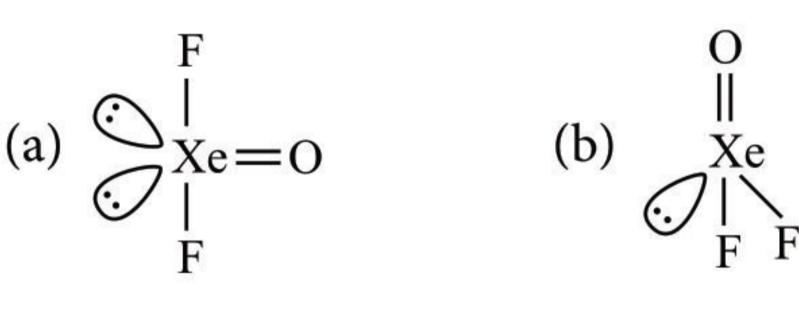
$$(Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-)$$

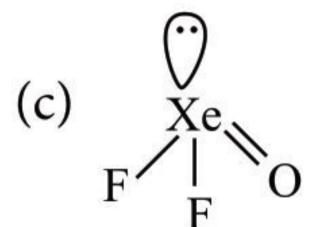
- (a) D > C > A > B (b) D > C > B > A
- (c) A > B > C > D (d) B > D > C > A
- 45. Which is the correct arrangement of the compounds based on their bond strength?
  - (a) HF > HCl > HBr > HI
  - (b) HI > HBr > HCl > HF
  - (c) HCl > HF > HBr > HI
  - (d) HF > HBr > HCl > HI
- **46.** For the reaction,

$$CH_3CHCH_2CH_3 \xrightarrow{H_2SO_4} CH_3-CH=CH-CH_3$$

$$CH_3CHCH_2CH_3 \xrightarrow{475 \text{ K}} CH_2=CHCH_2CH_3$$

- (a)  $CH_3 CH = CH CH_3$  predominates
- (b)  $CH_2 = CH CH_2 CH_3$  predominates
- (c) both are formed in equal amounts
- (d) the product ratio is dependent on the halogen *X*.
- 47. XeOF<sub>2</sub> has the following structure.





- 48. Which one of the following chlorohydrocarbons readily undergoes solvolysis?
  - (a)  $CH_2 = CHCl$

- (d)
- 49. Complete the following reactions by filling the appropriate choice.

(A) 
$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 +$$
 (i) + (ii)

(iii)

- (B)  $XeF_6 + 3H_2O \rightarrow$  (iii) + 6HF
  - (ii) (i)
- XeOF<sub>4</sub>  $H_2O$
- (b) 24HF XeO<sub>3</sub>  $3O_2$
- (c) 2HF  $2H_2O$ XeO
- (d) HF  $H_2O$  $Xe_2O_3$

- **50.** Arrange the given compounds in the order of decreasing boiling point.
  - Dibromomethane, bromoform, bromomethane, chloromethane
  - (a) Dibromomethane > bromoform
    - > bromomethane > chloromethane.
  - (b) Chloromethane > bromomethane
    - > dibromomethane > bromoform.
  - (c) Bromoform > dibromomethane >

bromomethane > chloromethane.

- (d) Bromomethane > chloromethane
  - > bromoform > dibromomethane.

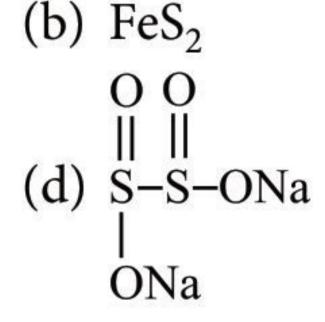
#### **CASE BASED**

## Read the passage given below and answer the following questions:

All the elements of group 16 have  $ns^2$   $np^4$  configuration in their outermost shell. Therefore, the atoms of these elements try to gain or share two electrons to achieve noble gas configuration. Sulphur and other elements of group 16 are less electronegative than oxygen, so, they cannot accept electrons easily. By sharing of two electrons with other elements, these elements acquire  $ns^2$   $np^6$  configuration and exhibit +2 oxidation state. Except oxygen, group 16 elements have vacant d-orbitals in their valence shell to which electrons can be promoted from p- and s-orbitals of the same shell. As a result, they can show +4 and +6 oxidation states also.

## The following questions are multiple choice questions. Choose the most appropriate answer:

- 51. Acidified solutions of sodium thiosulphate are unstable because in thiosulphate
  - (a) the two sulphur atoms are at unstable oxidation state of +2
  - (b) the two sulphur atoms are at different oxidation state of +6 and -2
  - (c) the S S bonds are unstable
  - (d) thio compounds contain S in oxidation state of zero.
- 52. In which of the following, the oxidation number of sulphur is −1 ?



**53.** In thiosulphuric acid  $(H_2S_2O_3)$ , the two sulphur atoms have the oxidation states

- (a) +2 and -2
- (b) +4 and -2
- (c) +6 and -2
- (d) +4 and +2
- 54. Like sulphur, oxygen is not able to show +4 and +6 oxidation states because
  - (a) oxygen is a gas while sulphur is a solid
  - (b) sulphur has high ionisation enthalpy as compared to oxygen
  - (c) oxygen has no d-orbitals in its valence shell
  - (d) oxygen has high electron affinity as compared to sulphur.
- 55. Which of the following are peroxoacids of sulphur?
  - (a)  $H_2S_2O_7$  and  $H_2S_2O_8$  (b)  $H_2SO_5$  and  $H_2S_2O_8$
  - (c)  $H_2S_2O_6$  and  $H_2S_2O_8$  (d)  $H_2S_2O_6$  and  $H_2S_2O_7$



#### Towards a COVID-19 breathalyzer for kids!

Currently, COVID-19 is diagnosed through the detection of specific viral nucleic acids or antigens, but these techniques are slow, relatively expensive, sometimes uncomfortable and prone to false-negative results. Scientists have observed that dogs can detect volatile organic compounds (VOCs) in human biological samples and distinguish certain diseases, including COVID-19. Researchers have also developed a sensor array to detect COVID-19-related VOCs in the exhaled breath of adults. Audrey Odom John and colleagues wondered if children infected with SARS-CoV-2 would also show changes in breath metabolites. If so, a breathalyzer-type device might someday quickly and comfortably screen large numbers of children in settings such as schools.

The researchers collected breath samples from children who were given routine COVID-19 tests prior to being admitted to the Children's Hospital of Pennsylvania for other conditions. Fifteen children were SARS-CoV-2 negative, whereas 10 tested positive. The team analyzed 84 VOCs in the breath samples by 2D gas chromatography and time-of-flight mass spectrometry, identifying six candidate biomarkers that were significantly elevated in the breath of children with COVID-19. Two of these markers (octanal and heptanal) were also elevated in the breath of adults with the disease, while the others were unique to infected children. Then, the researchers measured these VOCs in breath samples from a different group of 24 children, half of whom were positive for the disease. The six biomarkers could predict infection with 91% sensitivity and 75% specificity. These preliminary results suggest that breathalyzer testing could be an inexpensive, noninvasive, quick and sensitive alternative for the frequent screening of large numbers of children, the researchers say. Those who test positive could then be given more specific, nucleic-acid based tests to confirm the screening results.

## Read the passage given below and answer the following questions:

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular  $(S_N 2)$  and substitution nucleophilic unimolecular  $(S_N 1)$  depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards  $S_N 1$  and  $S_N 2$  reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent.  $S_N 2$  reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of  $S_N 1$  reactions.

## The following questions are multiple choice questions. Choose the most appropriate answer:

56. In the reaction given below:

$$\begin{array}{c} \text{CH}_3\text{CH}_2\\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_2\text{CH}_3\\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_2\text{CH}_3\\ \text{CH}_3 + \text{Cl} \end{array}$$

Which of the following statements is correct?

- (a) The reaction proceeds via  $S_N^2$  mechanism hence inversion of configuration takes place.
- (b) The reaction proceeds via  $S_N1$  mechanism hence inversion of configuration takes place.
- (c) The reaction proceeds via  $S_N^2$  mechanism hence their is no change in the configuration.
- (d) The reaction proceeds via  $S_N1$  mechanism hence there is no change in the configuration.
- 57. Among the choices of alkyl bromide, the least reactive bromide in  $S_N$ 2 reaction is
  - (a) 1-bromopentane
  - (b) 2-bromo-2-methylbutane
  - (c) 1-bromo-3-methylbutane
  - (d) 1-bromo-2-methylbutane.
- 58. Which of the following statements is not correct about  $S_N$ 2 reactions of alkyl halides?
  - (a) Nucleophile attacks the carbon from the side opposite to where the leaving group is attached.
  - (b) The bond formation and bond breaking take place in one step.
  - (c) The rate of reaction depends upon the concentration of nucleophile.
  - (d) S<sub>N</sub>2 mechanism is predominant in tertiary alkyl halides.
- **59.** Consider the following reaction:

$$\begin{array}{ccc}
CH_3 & CH_3 \\
 & | \\
 C_6H_5 - C - Br + H_2O \longrightarrow HO - C - C_6H_5 + HBr \\
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CHEMISTRY TODAY | SEPTEMBER '21

The reaction proceeds with 98% racemisation. The reaction may follow

- (a)  $S_N 1$  mechanism
- (b)  $S_N 2$  mechanism
- (c) E1 mechanism
- (d) E2 mechanism.
- 60. Which of the following is the correct order of decreasing  $S_N$ 2 reactivity?
  - (a)  $RCH_2X > R_2CHX > R_3CX$
  - (b)  $R_3CX > R_2CHX > RCH_2X$
  - (c)  $R_2CHX > R_3CX > RCH_2X$
  - (d)  $RCH_2X > R_3CX > R_2CHX$

#### **ASSERTION & REASON**

In the following questions (Q. No. 61 - 70) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- 61. Assertion: Ozone layer in the upper region of atmosphere protects earth from UV radiations of sun.

**Reason**: Ozone is a powerful oxidising agent as compared to oxygen.

**62. Assertion**:  $CH_3$ —CH— $CH_2CH_3$  on reaction with alcoholic KOH gives  $CH_3CH$  =  $CHCH_3$  as a result of dehydrohalogenation.

**Reason**: Elimination reaction takes place in accordance with Markownikoff's rule.

- 63. **Assertion**: SF<sub>6</sub> cannot be hydrolysed but SF<sub>4</sub> can be. **Reason**: Six F atoms in SF<sub>6</sub> prevent the attack of H<sub>2</sub>O on sulphur atom of SF<sub>6</sub>.
- 64. Assertion: Nucleophilic substitution reaction on an optically active halide gives a mixture of enantiomers.
   Reason: The reaction should be in accordance with S<sub>N</sub>1 mechanism.
- 65. **Assertion**: Fluorine combines with sulphur to form SF<sub>6</sub> but no other halogen form hexahalide with sulphur.

**Reason:** The reactivity of halogens increases as the atomic number increases.

**66. Assertion**: Replacement of –Cl group by –OH in chlorobenzene is easier if nitro group is present in the ring.

**Reason:** Nitro group leads to strengthen the C — Cl bond in chlorobenzene.

- **67. Assertion**: HClO<sub>4</sub> is a stronger acid than HClO<sub>3</sub>. **Reason**: Oxidation state of chlorine in HClO<sub>4</sub> is +7 and in  $HClO_3$  is +5.
- 68. Assertion: Boiling point of alkyl halides increases with increase in molecular weight.

**Reason:** Boiling point of alkyl halides is in the order RI > RBr > RCl > RF.

- 69. Assertion: Cl<sub>2</sub> gas bleaches the articles permanently. **Reason**: Cl<sub>2</sub> is a strong reducing agent.
- 70. Assertion: Bromobenzene upon reaction with Br<sub>2</sub>/Fe gives 1, 4-dibromobenzene as the major product. Reason: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

#### SOLUTIONS

- 1. (d): HNO<sub>3</sub> has nitrogen in its highest oxidation i.e., +5 state, due to this it itself gets reduces by oxidising other substances, hence is very strong oxidising agent.
- 2. (a)
- (d): Sequence of noble gases in periodic table: He, Ne, Ar, Kr, Xe, Rn.

4. (d): 
$$CH_3OH \xrightarrow{PI_3} CH_3I \xrightarrow{KCN} CH_3CN$$

$$X \qquad Y$$

$$CH_3COOH \xleftarrow{Hydrolysis}$$

$$Z$$

- (d): Because of high bond energy of N N bond,  $N_2$  is chemically inert.
- (d) 6.
- (d): Ionic radii increases down the group.
- (c):  $C_2H_5Br + KCN \longrightarrow C_2H_5CN + KBr$ Propane nitrile
- 9. (d): Ozone protects the earth's inhabitants by absorbing ultraviolet radiations.
- 10. (c)

H<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, HO
$$-$$
S $-$ S $-$ OH  $\Rightarrow$  3 $\pi$ -bonds  
O O

H

12. (d):

CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

CH<sub>3</sub>

- 2-Chloropentane has a chiral carbon atom.
- 13. (c): Neon gives brilliant orange-red glow in discharge tubes and is widely used for advertisement purposes.
- 14. (b):  $C_2H_5Cl + KOH_{(aq)} \longrightarrow C_2H_5OH + KCl$
- 15. (a)
- 16. (b) :  $CH_3Br + AgF \longrightarrow CH_3F + AgBr$ This reaction is known as Swarts reaction.
- 17. (d): All interhalogen compounds are diamagnetic in nature.
- 18. (b): (i) / will react faster because tert. carbocation / will be more stable.
- (ii) / will react faster due to greater stability of sec. carbocation.

19. (b): 
$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$$

$$Na_2S_2O_3 + Br_2 + H_2O \longrightarrow Similar reaction$$

$$Na_2SO_4 + 2HBr + S$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$
Different reaction

20. (c) : 
$$CH_3 - CH - C1 + 2Na + C1 CH_3$$
 $CH_3 - CH - CH_3 + 2NaC1$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $iso$ -Butane

- 21. (a) :  $2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$  $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$  $2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$  $2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$
- 22. (a): Side chain chlorination takes place by free radical substitution mechanism.
- 23. (b): Cane sugar on reaction with conc. HNO<sub>3</sub> gives oxalic acid.

$$\begin{array}{c} C_{12}H_{22}O_{11} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{11} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \ HNO_3 \quad} \\ C_{21}H_{22}O_{21} + 18[O] \xrightarrow{\quad Conc. \$$

24. (c)

25. (d): 
$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

26. (a): Allyl carbonium shows resonance and thus, allyl chloride is more reactive. Vinyl chloride does not show resonance and thus is less reactive.

27. (a): Sea divers carry a mixture of  $O_2$  and He when they go deep in the sea water.

**28.** (d):  $(C_2H_5)_3N$  may also be used for dehydrohalogenation of alkyl halide in place of alcoholic KOH or NaOH.

29. (d)

30. (c) : 
$$C_2H_5Cl + NH_3 \longrightarrow (C_2H_5)_4N^+Cl^-$$
  
(Excess) Tetraethylammonium chloride

31. (d): SO<sub>2</sub> is not a dehydrating agent.

32. (b):

H<sub>3</sub>C — CH<sub>2</sub> — C — CH — CH<sub>3</sub> 
$$\xrightarrow{aq. \text{ KOH}}$$
 — CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> OH

2,3-Dimethyl-3-iodopentane

$$H_3C - CH_2 - \overset{\circ}{C} - CH(CH_3)_2$$

$$CH_3$$

$$CH_$$

Racemic mixture

33. (c)

34. (b) : Cl 
$$\longrightarrow$$
 Br  $\xrightarrow{\text{Mg/ether}}$  ClMg  $\longrightarrow$  MgBr  $\xrightarrow{(A)}$  D  $\longleftrightarrow$  D  $\longleftrightarrow$  D  $\longleftrightarrow$  D<sub>2</sub>O

35. (a): Stability of hydrides decreases down the group due to decrease in bond strength (as the extent of overlapping between central atom and hydrogen decreases).

36. (c) : 
$$C_2H_5$$
 Br + Na  $OC_2H_5 \rightarrow C_2H_5 - O - C_2H_5 + NaBr$   
Diethyl ether

37. (a)

38. (b): 
$$CH_3$$
 $1$ 
 $1$ 
 $2$ 
 $3$ 
 $4$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

4-Bromo-3-methylpent-2-ene

39. (d)

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40. (d): 
$$O_2$$
 $Br_2/Fe$ 
 $Br_2/Fe$ 

 $-NO_2$  group is a deactivating and m-directing group so it directs the incoming Br– ion to the m-position thereby leading to the formation of m-bromonitrobenzene. Upon reduction with Sn/HCl, the  $-NO_2$  group reduces to  $-NH_2$  *i.e.*, the final product is m-bromoaniline.

**41. (b)** : 
$${}^{+3}_{2}O_{4}^{2-} < {}^{+4}_{SO_{3}}^{2-} < {}^{+5}_{2}O_{6}^{2-}$$

42. (d)

**43**. (d): SbH<sub>3</sub> will act as strongest reducing agent due to minimum bond enthalpy.

44. (a): Stronger base will replace Br most readily. Order of acidity is

AcOH > PhOH > H<sub>2</sub>O > CH<sub>3</sub>OH.

So, order of the basicity of their conjugate base is  $CH_3O^- > OH^- > PhO^- > CH_3COO^{-1}$ 

45. (a)

46. (a): This reaction gives the product in accordance with Saytzeff's rule.

$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CCH_5$ 
 $CCH_5$ 

**48.** (c): Solvolysis is related to the stability of carbocation formed and among these, benzyl carbocation is most stable. So, it will undergo solvolysis readily.

**49. (b)** : 
$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$
(i)
(ii)
(iii)
$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$
(iii)

**50.** (c): The given compounds are CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, CH<sub>3</sub>Br, CH<sub>3</sub>Cl. As molecular weight increases, boiling point increases. Order of boiling point is

$$CHBr_3 > CH_2Br_2 > CH_3Br > CH_3Cl.$$

**51.** (b): Acidified solution of sodium thiosulphate  $(Na_2S_2O_3)$  is unstable because in thiosulphate two sulphur atoms are in different oxidation state of +6 and -2.

**52.** (b) : In FeS<sub>2</sub> oxidation number of S = -1.

53. (c) : HO 
$$-S$$
 — OH;  $H_2S_2O_3$ , two sulphur atoms are

in -2 and +6 oxidation state.

54. (c)

55. (b):  $H_2SO_5$  and  $H_2S_2O_8$ 

**56.** (a): Inversion of configuration takes place in  $S_N 2$  mechanism.

57. (b)

58. (d): Tertiary alkyl halides are the least reactive in  $S_N2$  reactions because bulky groups hinder the approaching nucleophiles.

59. (a):  $S_N 1$  reaction proceeds with racemisation.

**60.** (a): Larger the number of alkyl groups at  $\alpha$ -carbon atom, more is the stearic hindrance and hence lesser the reactivity towards  $S_N 2$  mechanism.

61. (b)

**62.** (c): Elimination reaction takes place in accordance with Saytzeff's rule.

63. (a) 64. (a)

65. (c): The reactivity of halogens decreases as the atomic number increases.

**66.** (c) : Nitro group is an electron withdrawing group which leads to weakening of C — Cl bond, hence making it easier to replace the –Cl group.

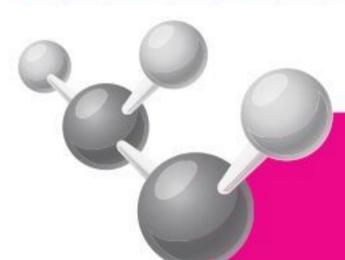
67. (b)

68. (b)

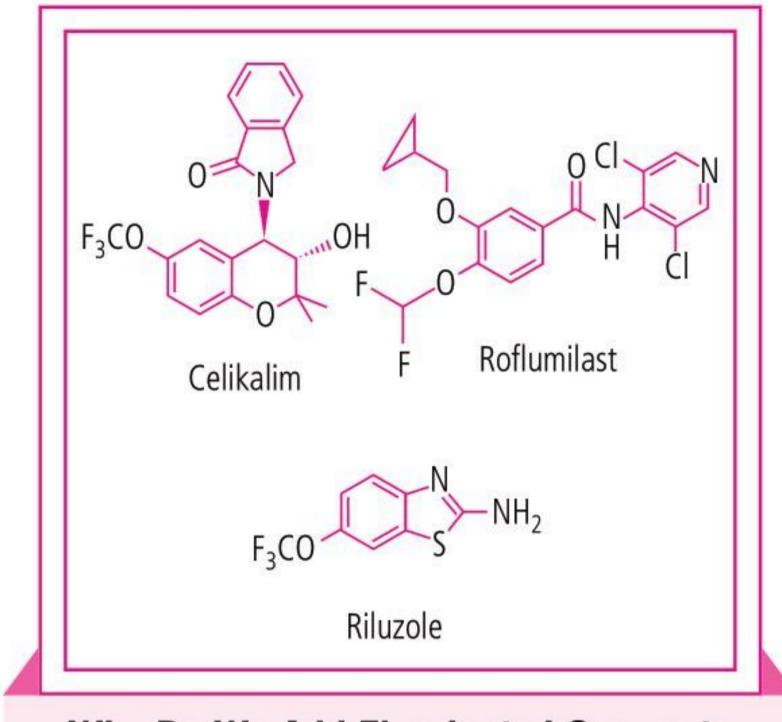
69. (c): Cl<sub>2</sub> is an oxidising agent. It bleaches the articles permanently by oxidation in presence of moisture.

**70.** (c) : Bromine in bromobenzene shows both -I effect as well as +M effect; but mesomeric effect dominates the -I character and becomes the directing factor for incoming electrophile.

Formation of electrophile:  $Br - Br + FeBr_3 \rightarrow Br^+ + FeBr_4^-$ Bromine acts as an *ortho-para* director for upcoming electrophiles.



# 3 Amazing Facts You Must Know



Why Do We Add Fluorinated Groups to Many Drugs?

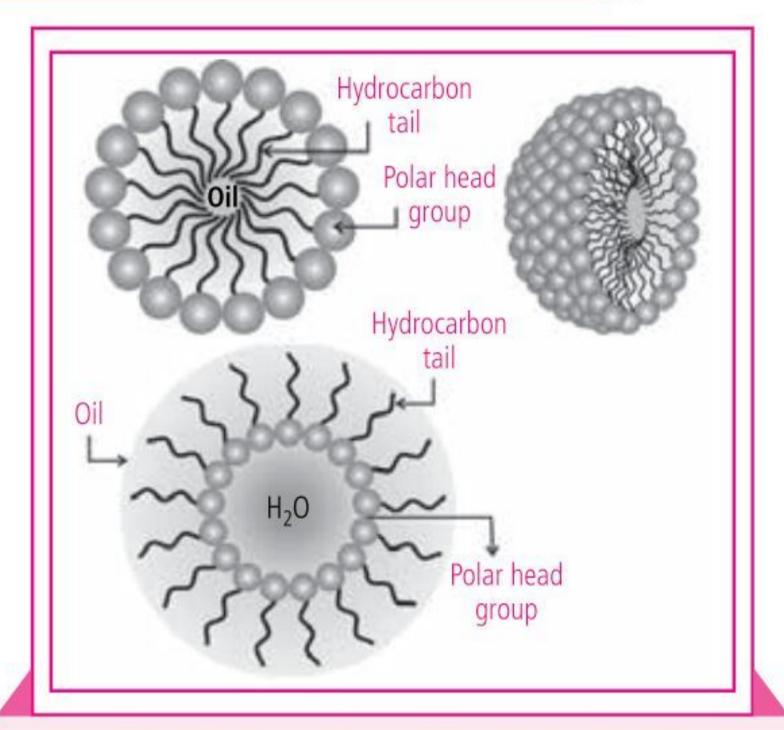
Sometimes you must have observed that F atom is common in drug design, which is weird because fluorine appears very rarely in naturally occurring molecules. Fluorine is an element that is usually added to drug molecules because it can increase its selectivity. Also, adding fluorine atoms increases the solubility of the drug in fats, making it easier for it to go through body barriers. Furthermore, the simple exchange of a H atom by a F atom in a certain position, makes it much more stable and less prone to degradation by oxidation. This may have a significant positive effect in the dosage of the drug.



#### **Recycled Olympic Medals**

There was a two-year national effort in Japan to collect enough recycled material to produce about 5000 bronze, silver and gold medals for the 2020 Tokyo Olympics. Up to 90% of Japanese cities, towns and villages participated by setting up donation pick-up sites, where hundreds of thousands of Japanese citizens donated their old electronic devices.

The recycling campaign produced 70 pounds (32 kg) of gold, 7,700 pounds of silver and 4,850 pounds of bronze, all from nearly 80 tons of small electrical devices such as old phones and laptops.



#### Why is Soap Used for Cleaning?

Soap is a mixture of amphipathic molecules, which have both a hydrophobic chain and a hydrophilic head. In water, these molecules such as fatty acid carboxylates are arranged forming micelles.

Micelles arrange the hydrophobic chains towards the centre, and the hydrophilic heads towards the outside (water). Hydrophobic molecules of dirt get "trapped" in the centre. This allows an easy removal of non-polar compounds from clothes or your skin.

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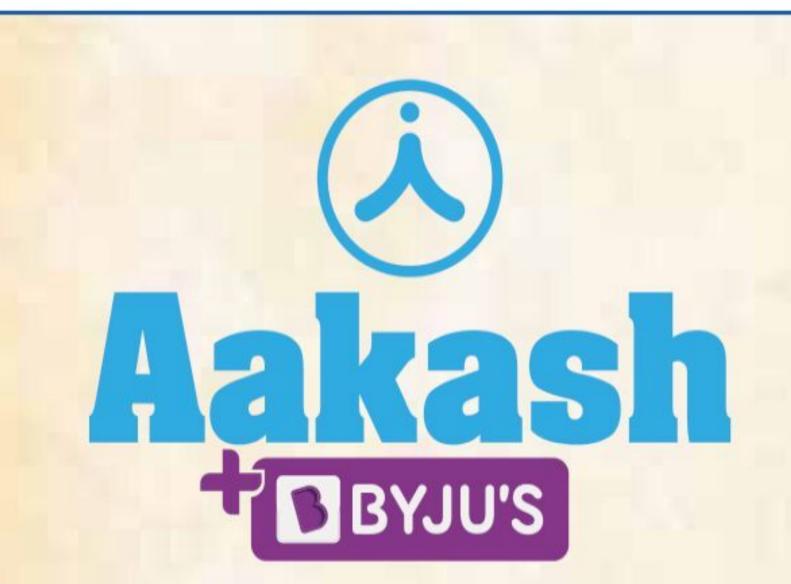
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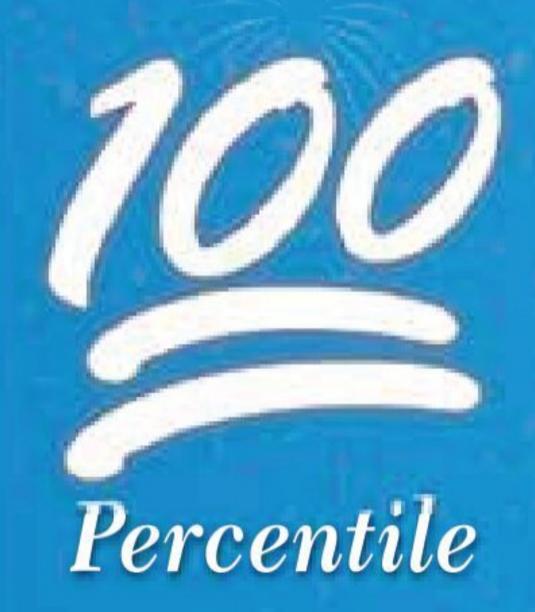














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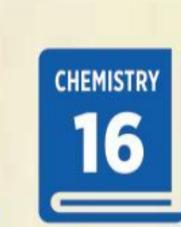


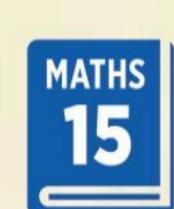
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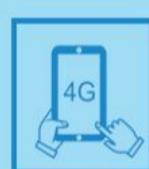
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